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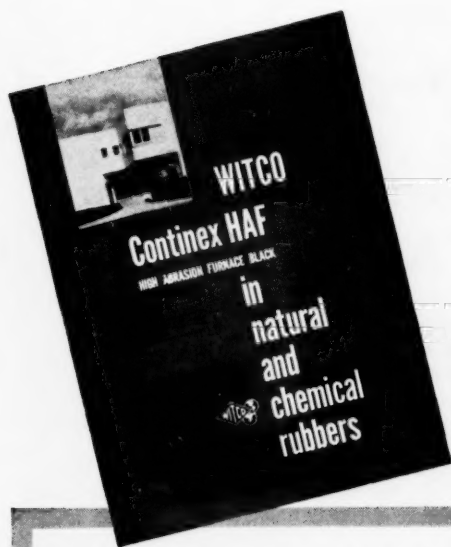
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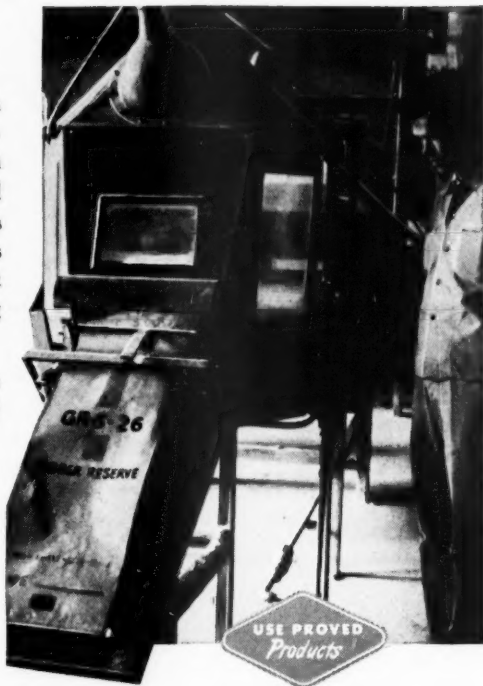
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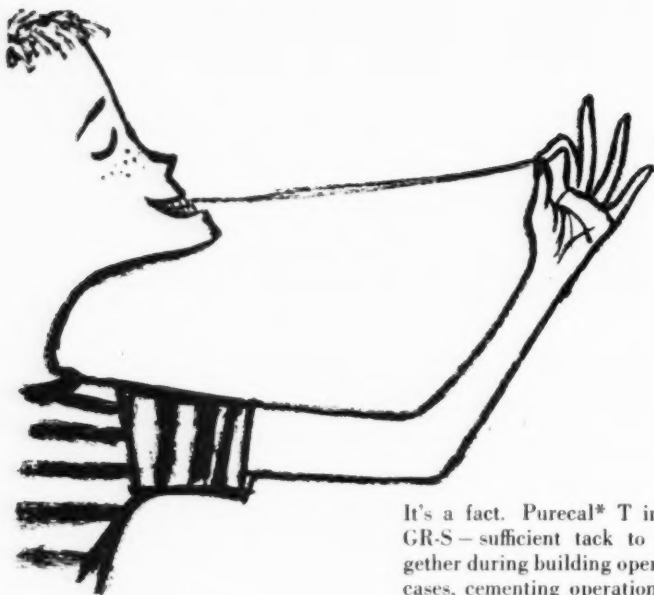


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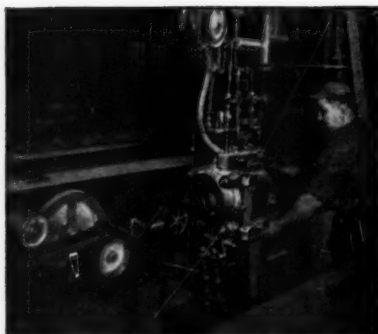
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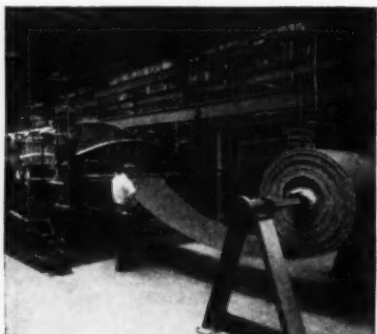
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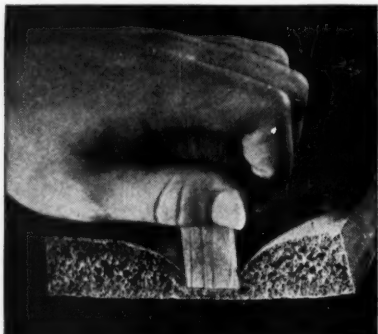
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RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXV

NUMBER 1



January-March, 1952

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Jan.-Mar., 1952

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RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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Chairman...C. L. KINGSFORD (Daval Rubber Co., Providence). *Vice-Chairman*...R. G. VOLKMAN (U. S. Rubber Co., Providence). *Secretary-Treasurer*...F. B. BURGER (Kleystone Rubber Co., Warren). (Terms expire at fall meeting 1952.)

SOUTHERN OHIO

Chairman...JACK FELDMAN (Inland Manufacturing Division, General Motors Corp., Dayton). *Vice-Chairman*...GEORGE LANG (Johnson Rubber

Co., Middlefield). *Secretary* . . . R. J. Hoskin (Inland Manufacturing Division General Motors Corp., Dayton). *Treasurer* . . . DAYLE BUCHANAN (Inland Manufacturing Division, General Motors Corp., Dayton). (Terms expire December 31, 1952.)

WASHINGTON, D. C.

Chairman . . . T. R. SCANLAN (Gates Rubber Co., Washington). *Vice-Chairman* . . . NORMAN BEKKEDAH (National Bureau of Standards, Washington). *Secretary* . . . GERALD REINSMITH (Army Office of the Chief of Ordnance Washington). *Treasurer* . . . PHILIP MITTON (Army Engineering Research and Development Laboratory, Washington). *Recording Secretary* . . . ETHEL LEVENE (Navy Bureau of Ships, Washington). (Terms expire October 1952.)

NEW BOOKS AND OTHER PUBLICATIONS

ADHESION AND ADHESIVES. N. A. de Bruyne and R. Houwink. Elsevier Publishing Co., Inc., New York and Amsterdam. 1951, cloth, $6 \times 9\frac{1}{2}$ inches, xv + 517 pages.— This book presents clearly and concisely the present state of knowledge on the theoretical and practical aspects of bonding diverse materials with animal glue, starches, dextrans, cellulose derivatives, synthetic resins, asphaltic bitumen, sodium silicate, latex, rubber solutions, ebonite, thermoplastic adhesives, isocyanates, and brass plating. The editors and the individual authors are to be congratulated on their presentation, and although there are points of detail which appear to be inconsistent, errors are few, and the book will be a very useful source of reference for some years.

The first part of the book deals with the theoretical aspects of the subject, the second part with the more technological aspects. In part I a real attempt is made to discuss adhesion problems in terms of fundamental concepts. This venture into the unknown is largely successful, and technologists should derive considerable benefit from the many practical hints given in the first four chapters.

The present reviewer welcomes this publication as the first book to survey the whole field of adhesion, and it is only the high standard attained throughout which gives prominence to the following inconsistencies.

Tables 23 and 24 (pages 243 and 244) contain information on the tensile and shear adhesion strength for various materials bonded with thermoplastic resin adhesives. It is misleading to quote tensile and shear adhesion strengths for natural rubber to hard rubber of 130 lb. per sq. in. and 190 lb. per sq. in., respectively. Much higher bond strengths can be obtained without using an adhesive if the stocks are properly compounded.

G. Salomon and W. J. K. Schonlau (Chapter 7) review fairly and completely the subject of rubbery adhesives but several statements give rise to confusion.

p. 408 "The bond (isocyanates) is to a certain extent thermoplastic"

p. 408 "The rubber-to-brass bond is definitely nonthermoplastic"

p. 409 "The isocyanate and brass bonds are moderately thermoplastic between 0–150°C"

The comments and analysis of Typly Q (p. 414) will interest many readers, but may be accepted with reserve by certain analysts. It is not clear (p. 414) how the results (Figure 148) were obtained for various thicknesses of Typly Q adhesive layer; much would depend on whether multiple layers were used or

whether the adhesive was deposited in a single layer in all cases, the latter method being preferable.

p. 417 "Further data on the vibration resistance of Vulcabond TX . . . awaited before its ultimate industrial value can be established"

Such data have been published in a paper which is quoted as reference 10d in this chapter.

The section on rubber-to-cord adhesion (p. 420) is the least satisfactory part of this chapter, probably because the authors compress rather intractable material into less than two pages. It is noted that the use of isocyanates for bonding rubber to nylon is omitted.

The chapter on physical testing (Chapter 9) gives a useful compilation of the different methods of testing, but the approach could have been more critical. As far as rubber adhesives are concerned, no mention is made of the importance of reducing the thickness of rubber to a minimum when testing the adhesive and choosing the thickness of the rubber to correspond to that used in service when testing actual rubber-metal units.

Statistics are mentioned throughout the book, but much more could and should be said in a second edition of the book. The bonding field is one where statistics can be extremely useful, especially in the planning of the experiment, but it should be remembered that statistical methods have their limitations and cannot be expected to produce worthwhile information from poorly organized experimental work.

The author propounds the doctrine (p. 464) that "the methods of statistical analysis do not relieve the experimenter from the responsibility of weeding out results that he knows to be wrong" and further asks that results should "accord with your common sense." The difficulty, of course, lies in the uncertain ground between "*knowing*" and "*believing*."

This excellent book has my wholehearted approval and recommendation, but leaves me convinced that for some time to come the true experimenter will be better advised to use statistical methods and a good measure of uncommon sense.

J. M. BUIST

ELEMENTS DE SCIENCE ET DE TECHNOLOGIE DU CAOUTCHOUC. Jean Le Bras. Société d'Editions Techniques Coloniales, Paris, France. Cloth 6½ by 10 inches, 354 pages.—At the request of the Council of the Institut Français du Caoutchouc, Dr. Le Bras, now Science Inspector General of this Institute and of the Institute in Indo-China, in 1941 set about organizing within the research center of the Institut Français a technical course designed chiefly for the training of rubber engineers. As a first step, an elementary course was set up to provide that basic knowledge of the science and technology of rubber required for participation in the advanced course of the I. F. C. and, incidentally, to fill a gap in the programs of most higher educational institutions of France.

The course was necessarily restricted to students of the Paris area; therefore, a condensed version of the course was arranged for the benefit of provincial students planning to go further; however, this still left them at a disadvantage with their Parisian fellows, and the Institute finally decided to publish, under the direction of Dr. Le Bras and with the aid of a number of technologists, the present handbook, which puts at the disposal of students everywhere in France

an exposition of all the material treated in the elementary course. Since the book also aims at filling the expressed needs of manufacturers, technologists in the provinces, and many persons of different educational backgrounds, all interested in rubber, it has been kept simple and direct so as to be as easy of comprehension as possible.

The oral part of the elementary course of the I.F.C. is amplified by lectures given by leading French authorities on current scientific and technological developments, and the work also utilizes their contents. A well-rounded survey of rubber is thus offered in the 15 chapters of the book, starting with the early history of rubber cultivation, manufacture, and research, and going on to the latest developments in these fields. The physical and chemical properties and structures of rubber and latex, tests and scientific theories, vulcanization, accelerators compounding ingredients, factory processing, and applications, are adequately discussed for the purpose of the work. Nor have synthetic rubbers been neglected. A list of French works on rubber, an index of authors quoted and a general index, complete the book.

As a matter of interest, we may mention the adoption in the book of a simplified method of representing organic structures which omits all C and H atoms which are dispensable, thereby to aid the student to memorize them and especially to facilitate reasoning by high-lighting the points of reactivity in the molecules (the double bonds, carbonyl and carboxyl groups, heteroelements). [From the *India Rubber World*.]

A PRACTICAL MANUAL OF RUBBER HARDNESS TESTING. By A. L. Soden. MacLaren & Sons, Ltd., Stafford House, Norfolk St., London, W.C.2, England. 6 × 8½ in. 50 pp. Price: 6s 6d (\$1.25 U.S. and Canada).—The series of articles by Dr. Soden on rubber hardness tests which were published in the *India-Rubber Journal* during the early part of 1951 has now been published in the form of a manual, with a rigid cover. The author first discusses the simple theory of indentation hardness tests and then, in turn, covers the standard tests, the factors affecting the design and use of hardness instruments, and the method of use and calibration of the more important instruments currently in use. In addition, relevant conversion tables are furnished in the form of appendixes and an extensive bibliography of 54 references is included. This is a practical manual which should prove of value to all those concerned with hardness testing of rubber. [From the *Rubber Age* of New York.]

THE SURFACE CHEMISTRY OF SOLIDS. S. J. Gregg. Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth, 5½ by 8½ inches, 306 pages. Price, \$8.50.—Emphasizing general principles throughout, this book presents a systematic survey of the different branches of the surface chemistry of solids. Instead of providing detailed descriptions of individual observations, the author treats this rapidly expanding field from the standpoint of fundamental principles. Adsorption, adhesion, spreading phenomena, catalysis, and related effects are all discussed as being the results of the presence of a field of force at the surface of the solid in its contact with a liquid gas, or another solid. While some branches of the subject are omitted, such as colloidal sols, electrode processes, and electrokinetic phenomena, the author succeeds admirably in his stated intention of presenting a brief but lucid survey of the field from the standpoint of practicability. The use of numerous tables and diagrams clarifies the text, and further study of the topics is suggested by the appending of literature references and bibliography lists to each chapter.

The book comprises 14 text chapters, a final chapter summing up the material presented, and both author and subject indexes. Following the introduction, separate chapters are devoted to adsorption of gases and vapors by solids; adhesion and the effect of adsorption; active solids; films on the surfaces of liquids; interpretation of the adsorption isotherm; the external surface of a solid, including porosity, permeability, smoke, and dust; the electron microscope and electron diffraction as applied to surface problems; friction and lubrication; spreading of a liquid over a solid; adsorption from liquids, including chromatography; determining the specific surface area, surface energy, and density of a solid; catalysis and chemisorption; and the part played by the surface in chemical reactions. [From the *India Rubber World*.]

THE STATICS OF THE TIRE. Compiled and issued by C. M. Sloman, 5777 Harvard Road, Detroit 24, Mich. $8\frac{1}{2} \times 11$ in. 45 pp. \$5.00.—There is no questioning the statement that tires of today represent a vast improvement over their predecessors. However, as measured against the performance of the vehicle, there is still room for improvement. The author of this treatise is of the opinion that if methods of calculation for what goes on internally in the tire structure can be developed, then the use of such methods can make attainable the optimum in tire performance. The treatise has for its purpose the evaluation of changes in contour of the various portions of the loaded pneumatic tire, the ultimate objective of the work being the calculation of stress-strain relationships in the materials of the tire. The author readily admits that this treatise can serve only as the groundwork for the mathematics of tire design. Nevertheless, the theorems offered for the distortion of inflated cylindrical envelopes under external loading and for inflation stress, cord paths, and deflection of the torus may be considered as a valuable tool which, in skilled hands, can help fashion the ideal in tire performance. This treatise should prove of extreme value to tire engineers in particular and to tire technologists in general. [From the *Rubber Age* of New York.]

COST OF MANUFACTURE OF ARTICLES FROM LATEX EBONITE IN COMPARISON WITH OBJECTS PRODUCED FROM RUBBER EBONITE AND BAKELITE. G. E. Rotgans and J. C. Gerritsen. (Communication No. 158.) Rubber-Stichting, Delft, Holland. $8\frac{1}{4} \times 11\frac{1}{2}$ in. 18 pp.—This report takes into account the fact that recent technical improvements in the manufacture of hard rubber objects by latex flow-casting have brought the economic potentialities of these methods into the foreground. With this in mind, a comparison was made between latex ebonite and rubber ebonite, the reference material being Bakelite. No other thermosetting plastics were included, since the mechanical properties of Bakelite most nearly resemble those of latex ebonite, and, for reasons of economy, Bakelite was considered to be sufficiently representative. Much of the information presented in this technical report is in the form of charts, graphs, and tables. (From the *Rubber Age* of New York.)

RUBBER'S HOME TOWN. By Hugh Allen. Published by Stratford House, Inc., 52 Vanderbilt Ave., New York 17, N. Y. $5\frac{1}{2} \times 8\frac{1}{4}$ in. 266 pp. \$3.75.—Although subtitled, "The Real Life Story of Akron," this book, the fifth volume of the American Heritage Series covering selected cities of America, is more aptly a story of people. Through its pages parade the long list of individuals who have written, and are still writing, the history of Akron.

The story of Akron is of course the story of rubber and accordingly the role played by rubber in the growth of the city since the turn of the century receives major attention, with special chapters devoted to The Age of Rubber, How Rubber Came to Akron, Goodyear and Firestone, Rubber Becomes Big Business, etc. Some of this history has been told before, but Hugh Allen's graphic style makes it all sound new and more interesting than ever. Before the reader is finished with the book he will understand why Akron is a more familiar name in faraway Rio de Janeiro and Singapore than even New York. The book has a foreword by Lloyd C. Douglas. There is also an appendix giving the story of Portage Path, biographical sketches of Akron personalities, and a chronology of Akron events. [From the *Rubber Age of New York.*]

PATENTS FOR TECHNICAL PERSONNEL. By Dr. Worth Wade. Chemonics, Inc., 400 Madison Avenue, New York 17, N. Y. 6 × 9 in. 44 pp. \$3.00.—Without footnotes, case histories, and legal terminology, this book simply and accurately discusses what a patent is, lists the steps which must be taken to protect an invention, discusses interference and prosecution of patents, describes a typical patent department of a company, and discusses its relation to the inventor-employee, etc. A most important, and so far neglected subject, is found in the last chapter: How to read a patent. Not only does this section clearly analyze the contents of a patent, but it presents a systematic method for analyzing and checking claims. A four-page pictorial section follows an invention from idea to patent. This handbook has been written for the inventor and employee of a chemical process plant. Its language is for laymen, not the patent attorney. In all, this book presents a complete, unobstructed picture of patents, their use and functions. [From the *Rubber Age of New York.*]

MODERN PLASTICS ENCYCLOPEDIA AND ENGINEER'S HANDBOOK: 1951: Published by Plastics Catalogue Corp., 575 Madison Ave., New York 22, N. Y. 8¼ × 11¼ in. 638 pp. \$2.00.—A drastic change in publication style has been made in this latest edition of the Modern Plastics Encyclopedia, the fifteenth to be issued. In order to make the book more directly useful to more people in the industry and among end users of plastics, the data which has become standardized through the years has been omitted, and the book now tells in detail what is new during the past year in plastics materials, applications, machinery, engineering and techniques. A special 40-page section is devoted to "Plastics in Defense." The directory section has been expanded in all departments and includes, for the first time, a section on Reinforced Plastics. Other valuable portions of the book include statistics of the industry, a plastics properties chart, and an extensive bibliography of reference books. [From the *Rubber Age of New York.*]

STATISTICAL METHODS FOR CHEMISTS. W. J. Youden. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. Cloth, 5½ by 9 inches, 136 pages. Price, \$3.—Characterized by a complete lack of statistical theory and proofs, this book presents an excellent exposition of the modern statistical system of units for expressing scientific conclusions. Drawing from his own lengthy experience in both the chemical and statistical fields, the author presents the statistical techniques which he himself found most useful in a wide variety of scientific investigations. Written from the laboratory worker's point of view, the book presents examples taken from actual data obtained in real

investigations, with explanations of the fundamental statistical principles behind these examples.

Introductory material has been held to a minimum because of the author's conviction that laboratory men have a real understanding of the meaning of their measurements, even though this understanding is usually inarticulate. Similarly, some topics usually included in statistics textbooks are either omitted entirely or else referred to only briefly because of their nonapplication to scientific experimentation. Subjects covered in the text include precision and accuracy; measurement of precision; the comparison of averages; resolution of errors; statistics of the straight line; analysis of variance; interaction between factors; requirements for data; arrangements for improving precision; and experiments with several factors. Appendices include a bibliography; tables of critical values; and a subject index. [From the *India Rubber World*]

PUNCHED CARDS, THEIR APPLICATIONS TO SCIENCE AND INDUSTRY. Robert S. Casey and James W. Perry. Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth, 6 by 9 inches, 514 pages. Price, \$10.—The accumulation of scientific and technical information, even in files of modest size, soon becomes unwieldy and presents difficulties in quickly finding any desired data. Considerable improvement in the speed and ease of finding information in files can be achieved by punched cards, either manually or machine sorted. This book, directed principally to the needs of the individual scientist or technologist, endeavors to present sufficient information to permit the application of punched card techniques to individual problems. At the same time a review of present knowledge and experience with punched cards is given to stimulate better use of available devices and the development of improved devices better suited to practical needs.

The book consists of 30 chapters, written by various authorities, and grouped into five sections. The first section, containing four chapters, is introductory and elementary in nature and presents sufficient information to permit an individual to set up and use a simple punched card system. The second section, comprising 14 chapters, consists of case histories of punched card applications, illustrating what has already been accomplished. The 10 chapters forming the third section are general and theoretical in nature; the chapter forming the fourth section is a study of the role punched cards and related devices may eventually play in coping with information problems. The concluding section is a chapter giving 276 references on punched cards for scientific information. Both subject and author indexes are appended. [From the *India Rubber World*.]

KINETICS AND MECHANISM OF ACCELERATED SULFUR VULCANIZATION *

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INTRODUCTION

In an earlier paper¹ on the kinetics of Buna-S vulcanization, the writer applied a new technique, that of adiabatic kinetics, to evaluate the rate parameters of that reaction. To this purpose he used data previously published by Bruce, Lyle, and Blake², on the time-temperature relationships during vulcanization. As stated in 1948, further experiments along the same lines, but extended to embrace accelerated vulcanization, were initiated by the writer but were unfortunately not completed, owing to unforeseen circumstances. An admirable paper containing rate measurements on the accelerated sulfur vulcanization of Butyl (GR-I) rubber has now appeared under the modest title "Stoichiometry of Vulcanization with Sulfur", by Zapp, Decker, Dyroff, and Rayner³. Once again it is possible to obtain from this paper kinetic parameters, indeed of remarkable accuracy, and the conclusions reached in the writer's first paper concerning the mechanism of sulfur vulcanization are thereby considerably strengthened and extended. As there appears to be a general neglect of kinetic interpretation of laboratory measurements (not to mention works practice!) in the rubber industry, some emphasis will here be laid on the kinds of information obtainable, or not obtainable, from a kinetic approach to the problems and observations peculiar to this branch of technology. A number of interesting theoretical parallels and differences will be brought out between sulfur vulcanization, the homogeneous polymerization of sulfur, and the acid-catalyzed cyclization of rubber, which are now reasonably thoroughly understood reactions.

THEORY OF VULCANIZATION KINETICS

The important conclusions of the paper mentioned in the opening sentence may be summarized by reference to the kinetic parameters in Table I, column 2, of the vulcanization of Buna-S with 6 per cent sulfur. The overall first-order nature of the reaction was derived with considerable reliability, and it was deduced from the values of X and n found, and from energetic considerations, that this overall first order reaction reflected the disappearance of the sulfur, whose concentration alone controls the rate of the reactions. The independence of the rate control from the polymer is supported by the fact that most rubbers, and indeed most low molecular weight model substances for rubbers, "vulcanize" with sulfur at comparable rates under similar conditions. It was confirmed from the first-order characteristics and the value of E and X found that the rate controlling step, in accordance with Meyer's hypothesis⁴, is the reaction:



* Reprinted from the *Journal of Polymer Science*, Vol. 7, No. 5, pages 485-498, November 1951.

TABLE I

Parameter	Unaccelerated Buna vulcanization	Butyl vulcanization, accelerated by TDED
Reaction order, n , overall	1	1 for first half of reaction, then rising
With respect to S	Believed 1	Same as overall
Arrhenius activation energy E , kcal.	32 (possibly 30.5-35)	23.0
Arrhenius frequency factor X , min. ⁻¹	1.9×10^{14} (possibly 2×10^{13} to 2×10^{16})	2.30×10^{10}
Unimolecular rate constant k , min. ⁻¹ $\times 10^3$		
At 140° C	1.4	12
At 180° C	45	150

It would be expected that for this simple unimolecular fission of sulfur ring to sulfur chain the activation heat would be equal to, or slightly higher than, the heat of reaction. Thus the value of $E = 32$ in Table I is in excellent agreement with the value of 27.5 ± 5 calculated for the heat of reaction (1) by Powell and Eyring⁵. The frequency factor X of 1.9×10^{14} was concluded to be in accord with reaction (1) as it is of the order of a molecular vibration frequency and because "no marked entropy (or 'steric') factor would be expected to slow down the proposed scission (1), since all the atoms or bonds in the S_8 ring are equivalent. Provided any one of the eight S atoms is sufficiently energized by collision, its two bonds would be strained before the energy is distributed around the ring". It may be added that if X actually turns out somewhat greater than the stretching frequency of an S—S bond in S_8 , this exaltation is no doubt attributable to the entropy increase in the transition state when the S_8 chain in process of formation gains considerable mobility over its parent puckered ring structure.

The exact details of the fast chain reaction that consumes the S_8 biradical, formed in (1), during the further course of the vulcanization reaction, and transforms it in the main to C—S—S—C cross links³, are not known. Nothing said about it below can be final, though the evidence is slowly building up into a coherent whole. The main testimony will continue to come from the structural work initiated by the Welwyn school, and kinetics has little to say concerning this subject at present. Thermochemistry reveals that the average S—S bond energy of an S_8 ring, i.e., one-eighth of the energy of the reaction $S_8 \rightarrow 8 S$, is about 64 kcal. in the gas phase⁶. It is significant that the first S—S bond broken in reaction (1), and whose scission triggers off the subsequent fast chain reaction, requires only about $E = 32$ kcal., because the S_8 is relatively stabilized by resonance⁵. In fact the high average energy of the S—S bonds in S_8 is due entirely to the high energy, probably as high as 102 kcal.⁷, required to split each of the four S_2 molecules contained in an S_8 ring into its two S atoms. It is thus perhaps not surprising that Zapp and coworkers find in the main S—S fragments as the cross-linking entity, though if these are formed from mercaptyl radicals they do not necessarily correspond to fragments performed in an original S_8 ring. While the first ring opening scission (1) "borrows" its 32 kcal. in the form of actual energy of activation from the Maxwellian energy distribution, the fast scissions of the remaining S—S bonds, and the disappearance of C=C unsaturation, must "pay their way" by the formation of C—S bonds, and possibly C—C bonds. This seems quite feasible, since the formation of a C—S

single bond liberates about 64 kcal.⁶ We may picture the "depolymerization" of the sulfur during these fast stages to reduce the sulfur chain atom by atom, *e.g.*:



A very similar sulfur chain degradation step was, in fact, suggested by Farmer and Shipley⁸.

We have assumed so far that each S_8 ring splits and is then consumed rapidly by some such interaction with the rubber as the typical reaction (2). Thus we have excluded any interaction between sulfur chain radicals and sulfur rings, such as obviously occurs in the homogeneous polymerization of molten sulfur⁶. The theoretical reason why the reaction chains in vulcanization should be confined to one S_8 ring and its successor chain fragments is that the vulcanization system is a very dilute sulfur solution and the sulfur chain radicals disappear by the fast reaction with the rubber before they stand much chance of encountering another unreacted S_8 . The overall first-order kinetics of vulcanization provides the experimental sanction for the theory, and this is rendered more precise by the demonstration, given below on the basis of the data by Zapp and coworkers, of first-order kinetics with respect to sulfur. The only way in which such kinetics could be reconciled with a reaction chain affecting several (say r) S_8 rings at a time is through the unlikely assumption that r is proportional to the amount of sulfur present at any stage of the reaction. In this connection it is worth recalling that H_2S markedly lowers the viscosity of polymerizing sulfur⁵, and action that may be ascribed to its functioning as a chain-transfer agent comparable to the function of thiols in olefin polymerization. H_2S also catalyzes the addition of sulfur to rubber and other olefins⁹, possibly an analogous chain transfer action from one S_8 ring to another through a sufficiently long-lived radical. In this way the acceleration by HS_2 may perhaps be fitted quite innocently into the theory of accelerator action developed below.

THEORY OF ACCELERATOR ACTION

The most important, though not the only industrially important, factor concerning accelerators of vulcanization is that implied in their name. It is the one on which kinetics has most to say, and on the general kinetic theory of sulfur vulcanization outlined in the last section it is possible to predict qualitatively the kinetic parameters inherent in the measurements by Zapp and coworkers, which will be considered in the following section. For in general a catalyst can only appreciably accelerate a complex reaction by providing a faster alternative for its slowest step, or some sequence including the slowest step. In sulfur vulcanization the slowest step is the very first, and is such that, without it, no chemical action of sulfur in the form of S_8 is possible. Accordingly, any acceleration of the reaction as a whole must necessarily consist in a speeding up of this first step, which splits the ring open. This could in principle be done through an increase in X , or a decrease in E , or both. From the meaning attributed to the values of these two parameters listed in column 2, Table I, there is little scope for increasing X , the vibration frequency of the $\text{S}-\text{S}$ bond, but considerable scope for decreasing E in reaction (1). The latter reaction produces two free radical ends in an S_8 biradical chain, while the essential chain propagation step (2) only requires one free radical end, so an opportu-

ity exists for one end to be involved in an energetically favorable bond formation. If we recall that the accelerators used by Zapp and coworkers give radicals of the type $R_2N-CS-S\cdot$ and that sulfur is very prone to attack by free radicals¹⁰, indeed that its homogeneous polymerization depends on such an attack by a radical (the biradical $\cdot S-S-S-S-S-S-S-S\cdot$) ending in $-S\cdot$, then the following equation, involving an attack of an accelerator radical Z on the sulfur ring, seems a plausible key to the problem of accelerated vulcanization:



The question arises how the essential kinetic parameters may be expected to change, apart from the desired decrease in the activation energy, when (3) instead of (1) sets the chain reaction in motion. It is immediately clear that necessity of bringing Z (present in small concentration) into a favorable collision with S_8 represents a steric requirement which must lower considerably the frequency factor X of the appropriate rate constant, when compared with the purely thermal unimolecular splitting (1). Theory accordingly requires that the effect of an accelerator must be due to a decrease in E large enough to outweigh the decrease in X to be expected. This may be stated by saying that accelerators should be relatively more effective at lower temperatures, a fact in general agreement with practical experience. The simplest prediction concerning the overall reaction order n , when the bimolecular reaction (3) takes over the business of (1), might appear to be the assumption of a second-order reaction, first order in the sulfur, and first order in Z. It must be remembered, however, that Z will in turn depend on the accelerator concentration, and Z will be regenerated at the end of the fast reaction chain that leads to the consumption of the sulfur contained in the radical $Z-S-S-S-S-S-S-S-S\cdot$ by formation of $C-S-S-C$ systems with the rubber. While the precise mechanism of this regeneration must be left open at present, it may clearly lead to a stationary concentration of Z throughout the vulcanization reaction, depending only on the initial accelerator concentration. The overall reaction order would thus still be unity, owing to the first-order disappearance of the sulfur only. If the regeneration of the accelerator is not quantitative, *e.g.*, if the accelerator is slowly consumed in side reactions, the overall reaction order would rise above unity. These notions will now be tested by reference to the kinetic data extracted from the work of Zapp and coworkers.

EVALUATION OF KINETIC DATA PROVIDED BY ZAPP AND COWORKERS

These authors present their results³ partly in the form of graphs and partly as tables. Only the six runs tabulated, three at different temperatures for tellurium diethyldithiocarbamate (TDEDC) and three at corresponding temperatures for tetramethylthiuram disulfide (TMTDS) will be analyzed here because of the greater accuracy inherent in tabular data. It should be pointed out, however, that Zapp's graphs are drawn on logarithmic paper, so that effectively the percentage of combined sulfur is plotted against the logarithm of the time. The convenient plot for the kinetic analysis of a first-order disappearance of sulfur is $\log S$ against time t , where, moreover, S represents the percentage of sulfur remaining free. Such plots are shown in Figures 1 and 2 of this paper. Probably owing to the bias inherent in their method of plotting, Zapp and coworkers speak of an induction period; while the excellent extrapolation of our plots through the point $t = 0$, $\log S = 2$ (*i.e.*, 100 per cent free

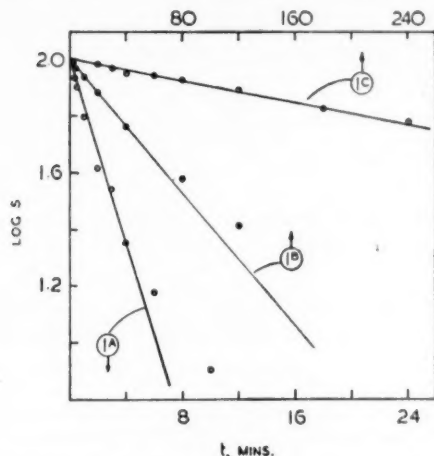


Fig. 1.—Unimolecular plot of Butyl vulcanization (TDEDCl).

sulfur), proves that there is no kinetic basis for any induction period. This matter is important, since induction periods undoubtedly do occur in the first-order vulcanization reaction between natural rubber and S_2Cl_2 in solution¹¹, where they remain unexplained, and in the cyclization of rubber latex¹², where they may possibly be associated with diffusion effects.

Table II summarizes the relevant experimental data of the six runs (whose rate results are listed in Zapp's Tables II and III), and Figures 1 and 2 present plots of $\log S$ against t as a test for first-order characteristics. The temperatures employed in each figure span the considerable range of about 83° K. At the highest temperature the runs are followed until over 90 per cent of the sulfur originally present has been consumed, while at the lowest temperature only

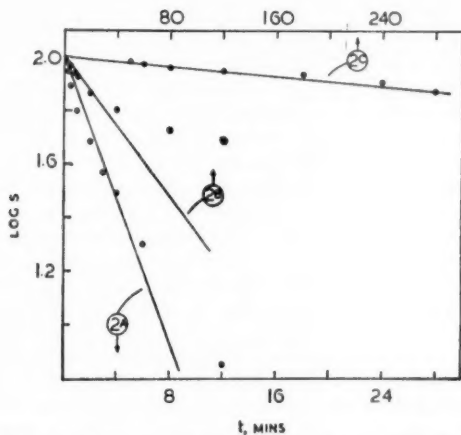


Fig. 2.—Unimolecular plot of Butyl vulcanization (TMTDS).

TABLE II

Temperature, °F °K	Fig. 1 Graph			Fig. 2 Graph		
	1 ^A	1 ^B	1 ^C	2 ^A	2 ^B	2 ^C
	400 477.5	300 421.9	250 394.2	400 477.5	300 421.9	250 394.2
Butyl rubber (GR-I), 0.89% un- saturation	100			100		
Zinc oxide	5			5		
Tellurium diethyldithiocarbamate	1.55					
Tetramethylthiuram disulfide				1		
Sulfur	2			2		

25–41 per cent of the sulfur disappearance is covered. Accordingly, deviations from a first-order law will be more readily apparent at the higher temperatures.

THE REACTION ORDER

Inspection of graphs 1^C and 2^C at 250° F reveals their excellent linearity, so the reaction is there represented by a first-order equation with high accuracy. This is particularly noteworthy in 1^C, where the nine experimental measurements of free sulfur (including the time zero) cover the consumption of 41 per cent of the sulfur originally added, and yield a regression line of $\log S$ on t , with a correlation coefficient 0.9987. The slope of the line yields a first-order constant of 0.002207, and statistical investigation shows that a slope differing by more than 0.00015 from this figure would, on average, be found only once in a hundred repetitions of this experiment by Zapp and coworkers. The amount of experimental scattering of the points about this line could readily be accounted for by occasional temperature fluctuations alone, since the degree of control claimed by the authors is only $\pm 2^\circ$ F. The general smoothness of our plots indeed suggests that the temperature control within most of the individual runs was actually better than suggested by these limits. The remaining runs 1^A, 1^B, 2^A, and 2^B, at the higher temperatures, all exhibit some curvature in the same sense, *viz.*, toward a higher reaction order. With 1^A and 1^B, accelerated by TDEDc, this curvature is seen to be due only to the last two points of each plot, which lie in the range between 62 and 92 per cent consumption of the sulfur. On the other hand, in runs 2^A and 2^B, accelerated by TMTDS, the curvature is stronger and visibly not confined to the end of the reaction only. A second-order plot would give a good fit to 2^B, the run showing the highest reaction order. In interpreting the evidence on reaction order just summarized, the first comment is that the overall first order observed at 250° F, and over the major part of the reaction in presence of TDEDc at all three temperatures, undoubtedly reflects the disappearance of the sulfur, as is here directly confirmed by chemical analysis. In the vulcanization of Buna-S, the same conclusion has been made plausible¹ by theoretical arguments in the absence of analytical data (*cf.* Table I, column 3, under reaction order). As regards the incursion of higher reaction orders at higher temperatures, this effect is most likely to reflect a progressive decline in the concentration of the radical Z, or possibly of the reactive sites in the polymer. In view of the earlier onset and more marked nature of the higher order reaction in the presence of TMTDS, it is most significant that Zapp and coworkers bring forward theoretical and practical evidence for the fact that TMTDS, unlike TDEDc, reacts appreciably with the reactive sites in the polymer, thus blocking them for vulcanization. This parallelism considerably strengthens the kinetic analysis here presented.

The choice of Butyl by Zapp for his vulcanization studies was motivated by his desire to "satisfy all the potential points of cross-linkage while still possessing a network that is soft and elastic". The Butyl rubber used had, in fact, only about 1.2 per cent of such points when compared with Buna-S. The choice of Butyl is most felicitous from the kinetic viewpoint, since it provides a severe test for any participation of the polymer in the rate determining process. Theoretical reasons were advanced earlier¹ for discounting such participation in Buna-S vulcanization, where the reaction order is not a sensitive experimental test, because only a small fraction of the potential points of cross-linking are actually reacted. With Butyl rubber such reaction is practically quantitative, and our present analysis shows that such participation of the polymer in the measured rate is at most confined to the higher temperatures, and in presence of TDEDc to the last third of the reaction. While the evidence is less clear-cut in the case of TMTDS acceleration, the similarity of the Arrhenius parameters for the two accelerators, discussed in the next section, renders quite unlikely the assumption of any radical difference in mechanism over the early part of the reaction. It is concluded that reaction steps involving collision with the polymer do not determine the rate of sulfur vulcanizations, except just possibly at the end of a particularly searching reaction. The classification of polymer reactions from this viewpoint of rate control involving, or not involving, the polymer itself, is of technical significance as explained in section V.

THE ARRHENIUS PARAMETERS

The comparison of initial unimolecular constants, from the initial slopes of the 6 lines in Figures 1 and 2, forms a good basis for a theoretical treatment of the influence of the temperature on the reaction rate. The usual Arrhenius plot (Figure 3) for these constants referring to Figure 1, *i.e.*, for acceleration by TDEDc, gives a most satisfactory linearity, which in itself lends support once again to the interpretation of vulcanization in terms of chemical kinetics. As explained below, the rate constants for TMTDS do not significantly differ from those for TDEDc, so a separate Arrhenius plot is not necessary. The activation energy for TDEDc calculated from the slope and the frequency factor from the intercept of Figure 3 are listed in column 3 of Table I, while column 2

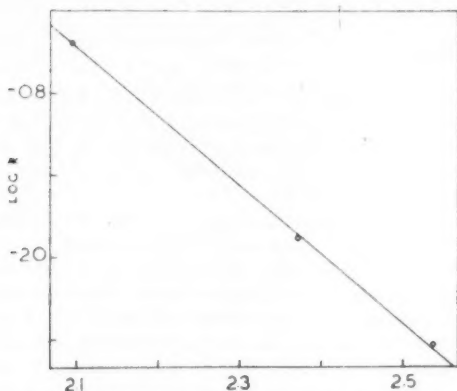


FIG. 3.—Arrhenius plot of Butyl vulcanization (TDEDc). Abscissa is $10^3/T$.

shows for comparison the values referring to the unaccelerated vulcanization of Buna-S. Table III presents the significant experimental differences between these two vulcanizations, and the effects which each of these differences alone will be expected to have on the vulcanization rate in the light of our theories and relevant known facts. The balance of effects expected, necessarily a rough figure at best, is struck at the foot of the table and compares admirably with the experimental data in Table I. As deduced from the theory in part III, moreover, the net acceleration is precisely due to a large decrease in E , from 32 to 23 kcal., outweighing a decrease in X by about a factor of 10^4 (Table I). The observed reaction order has just been shown to agree with the theory, which now rests on a substantial body of observations and quantitative data. Probably the most important work outstanding now is to chart the effect of varying initial concentrations of TMTDS on the rate of sulfur combination. If Equat-

TABLE III

Unaccelerated Buna-S vulcanization	Accelerated Butyl vulcanization	Expected effect on rate of sulfur combination
Hydrogen only on C=C	Isoprenic methyl groups	No effect, as polymer not involved in rate controlling step
75 mole-per cent unsaturation	0.89 mole-per cent unsaturation	No effect, for reason as above
Buna-S rubber as reaction medium	Butyl rubber as reaction medium	Very small effect, as radical reactions are not sensitive to small changes in medium
Absence of ZnO	Presence of ZnO	No effect, as ZnO not involved in rate control. ZnO is known not to have any effect on rate of S combination ⁹
Absence of accelerator	Presence of accelerator (TDED 1.55%, or TMTDS 1%)	The presence of accelerator, from general works experience, would increase the rate by about one power of ten at 140° C
6% S	2% S	No effect when rate is expressed as unimolecular constant
Hence net effect on rate expected		One power of ten approx. at 140° C
Net effect on rate found (Table I)		9-fold at 140° C

tion (3) is a correct explanation of accelerator mechanism, and if it operates through a small stationary concentration of $(\text{CH}_3)_2\text{N}-\text{CS}-\text{S}\cdot$ radicals, then it may be predicted that the initial rate at a sufficiently low temperature (say 250° F) to eliminate the purely thermal reaction (1), should vary as the square root of the TMTDS concentration.

Zapp and his coworkers presented data for only one concentration of each of the two accelerators used. The concentrations were chosen to contain the same amount in moles of $\text{R}_2\text{N}-\text{CS}-\text{S}\cdot$. It does not follow, of course, that the same stationary concentration of these radicals exists in the free state under these conditions, though this hypothesis certainly explains Zapp's results brilliantly. Table IV confronts the measured rate constants, obtained from the slopes of the lines in Figures 1 and 2, respectively. It is seen that while these rates vary altogether over a range of about 300, the agreement between the rates at any one temperature, using either one part of TMTDS of 1.55 parts

TABLE IV

Temperature	Unimolecular initial rate constants $\times 10^4$	
400° F	3700 TDED	3000 TMTDS
300° F	135	150
250° F	22.1	10

of TDED, are equal to within a factor of 2.3. This provides a dramatic confirmation of the kinetic equivalence of these two accelerators used in these precise proportions.

THE TECHNOLOGICAL IMPORTANCE OF THE RATE CONTROLLING STEP

With reference to the entry under ZnO in Table III, it should be noted that Zapp and his coworkers have charted the technologically very important fate of the sulfur, as it becomes bound, partly organically to the rubber, and partly inorganically to the zinc oxide. In accordance with the mechanism expounded, these two reactions, however important, do not influence the rate as neither the rubber nor the zinc oxide enters the rate-determining change (3). This state of affairs endows both the technological practice and the kinetic analysis with a valuable simplification, but it also points to the limitations on the fundamental information obtainable from kinetic analysis under just those experimental conditions which are technically useful.

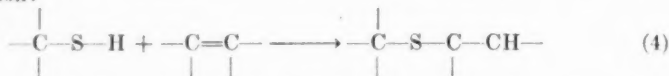
In the acid-catalyzed cyclization of natural rubber latex, the rubber does without any doubt¹² enter the rate determining step. As a result, the first effect of Table III, *viz.*, the introduction of isoprenic methyl groups alone, which can be realized by passing from G-RS to natural rubber in this reaction, leads to an increase¹³ in rate of probably 10^5 or more. In fact, due to the absence of the electron repelling (*i.e.*, proton attracting) effect of the isoprenic methyls, the cyclization of GR-S on a practical scale has been beset with great difficulties¹⁴. In further illustration of the effect of substrate on rate, provided the substrate enters the rate controlling process, the cyclization of a diisoprenic terpene can be speeded up by a further factor of about 10^7 over that of rubber (10^{12} over that of GR-S) by substitution with a $\text{CH}=\text{CH}-\text{CO}-\text{Me}$ group in a strategic position as in pseudoionone¹⁵. The varying success of the rubber technologist in extending chemical reactions from one substrate to another can thus be explained kinetically. Vulcanization can be easily extended, but cyclization only with difficulty, because the rubber substrate enters the rate-determining step in the second, but not in the first reaction.

INTRAMOLECULAR CYCLIZATION AND INTERMOLECULAR CROSS-LINKING

It is interesting to note that we gain in topochemical regularity of the acid-catalyzed cyclization what we sacrifice in generalizability of the reaction. Contrary to what has often been believed in the past, an isoprene unit in this reaction forms a ring closing bond neatly with one of its neighbors in the same chain, rather than with more distant units in the same chain, or with a unit in another chain¹². The reason is that if the cyclization with a neighboring unit proceeds only 10^3 times faster than with a more distant one, then it will constitute the only reaction detected in practice. This is not an unreasonable condition, considering small structural changes such as substitution with Me and with $\text{CH}=\text{CH}-\text{CO}-\text{Me}$ can speed the reaction by factors of 10^7 and 10^{12} ,

respectively. A sketch of the coiled rubber molecule¹⁵ shows convincingly why the nearest isoprenic neighbors might, in fact, react considerably faster in acid catalyzed cyclization. The writer has stressed the importance of studying cyclization rates from the proper viewpoint of statistical theory, which supercedes, in a sense, the Bayer strain concept in large rings.

In sulfur vulcanization, intramolecular cyclization reactions are thought to consume, under certain conditions, some of the sulfur which the technologist wishes to utilize as far as possible for cross-linking purposes. With Butyl rubber this cyclization cannot occur because the isoprene units are spaced out, on the average, by 100 isobutene groups. For polyisoprenes proper, however, the polar addition:



has been suggested by Naylor, on the basis of structural investigations, as the chain-terminating step. Now this step has also been shown by him to lead to intramolecular cyclization, rather than cross-linking, in the case of the diisoprenic dihydromyrcene (methylgeraniolene)¹⁶ while, the reverse is predominantly true for rubber. This contradictory behavior was attributed by him tentatively to the "purely physical intermolecular entanglement of the long rubber molecules". But, as we now know, this entanglement does not prevent rubber from cyclizing under acid catalysis exactly analogously to methylgeraniolene or geraniolene, and indeed at comparable rate if allowance is made for the electronic effect of the substitution pattern¹⁷. It is reasonable to conclude that (4) is not the most important cross linking step in rubber vulcanization. It is suggested that the step:



is a more likely candidate for three reasons. It follows naturally on from (2) without requiring any hydrogen capturing step; it accounts for Zapp's finding of two sulfur atoms in the average cross-link; and it accounts readily for the preference of intermolecular over intramolecular linking. For it to occur intramolecularly, (5) would require simultaneously the presence of two $-S\cdot$ radicals on adjacent isoprene units, a most unlikely occurrence, and then the formation of a seven-membered ring.

Vulcanization, as a random cross-linking process, is topochemically less simple than the regular intramolecular cyclization of neighboring units. Nevertheless, certain kinetic regularities affecting the fast steps in vulcanization have been observed, and are consistent with the advocated mechanism. Certain observed irregularities, however, need explanation, as they do not fit the mechanism so readily. As stated by the writer¹, the application of the adiabatic technique to Buna-S vulcanization "is favored by the circumstance that the simple primary act is followed by a chain of reactions, which—however complex—liberate on the average a constant amount of heat. This conclusion is supported by the known facts that the unsaturation and the heat of vulcanization change linearly with the amount of sulfur employed". The runs at 250° F by Zapp and his coworkers, which, as shown above, fit a first-order sulfur decay so admirably, also exhibit related regularities concerning the subsequent steps:

(1) The fractional distribution of the combined sulfur between the organically bound sulfur and zinc sulfide is constant throughout the reaction. In 2° this is rigidly true within experimental error, *viz.*, everywhere within ± 0.01

per cent of organically bound sulfur out of a total of 0.25 per cent. In 1°C agreement is still satisfactory, though only about one-third as good.

(2) The number of cross-links, determined by equilibrium swelling experiments, varies all but proportionally to the sulfur combined.

Both (1) and (2) readily fit the proposed mechanism, as they are translated thus: The rates of all the steps are determined by the S_8 splitting rate (proportional to free sulfur), while the ratio of the rates of subsequent steps is independent of all concentrations. In the runs at higher temperature by Zapp and his coworkers first-order characteristics are lost sooner or later in the reaction, and neither (2), nor particularly (1), hold. At 400°F , the swelling experiments suggest, in fact, that the number of cross-links go through a maximum during the sulfur combination, a reversion effect attributed to disulfide splitting. In an earlier paper¹⁷, Zapp deduced that the rate of cross-linking goes through a sharp maximum during vulcanization. In this connection he mentioned very tentatively a chemical kinetic scheme, but as this is not in accordance with the later facts that support the mechanism here advanced, it appears likely that reversion was responsible for these rate maxima also.

SUMMARY

As a step in the general development of a kinetic theory of sulfur vulcanization, rate data published by Zapp and coworkers on the accelerated vulcanization of Butyl rubber are analyzed. Rate constants are calculated, some with remarkable accuracy, and these compare admirably with those previously calculated by the writer from data on unaccelerated Buna-S vulcanization by Blake and coworkers. In accordance with theory, acceleration is found to be due to a decrease in activation energy, which more than compensates for a considerable decrease in frequency factor predicted by theory. As in the case of unaccelerated cure, the reaction order is unity, at least initially, and reflects the disappearance of the sulfur during the reaction. The rate determining step is the reaction:



where $\text{Z} \cdot$ is a radical derived from the accelerator. Although the sulfur combines with the polymer and with zinc oxide, these two entities thus do not enter into the rate-controlling step. The importance of classifying polymer reactions according to the participation or nonparticipation of the polymer in the rate control is stressed. Tentative arguments are advanced for kinetic and chemical details of the chain reaction between $\text{Z}-\text{S}-\text{S}-\text{S}-\text{S}-\text{S}-\text{S}-\text{S}-\text{S} \cdot$ and rubbers. Some parallels are drawn between vulcanization, polymerization of sulfur, and the cyclization of rubber.

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THE MOLECULAR STRUCTURE AND PROPERTIES OF RUBBER *

V. I. KASATOCHKIN AND B. V. LUKIN

The molecular structure of rubber resembles that of liquids, which have a characteristic distribution of linear-chain molecules, united by transverse van der Waals forces. The x -ray diffraction diagram of undeformed rubber shows a diffuse ring, the characteristic diffraction spectrum of liquids, and this is accepted as experimental proof of the similarity between rubber and liquids. The theory that the structure of rubber involves reactive bonds in the adjacent molecular chains at short distances apart is not in accord with the relatively free rotation of these chains, which is manifest by the elastic properties of rubber, and the theory in no way distinguishes unvulcanized rubber from straight-chain paraffins.

A straight-chain molecular system in which most of the links of adjacent chains are cross-bridged by van der Waals forces is a fairly rigid system, with relatively little molecular motion. The rotation of the links is equivalent to rupture of the van der Waals bonds, and in no way corresponds to the observed high degree of motion of the molecular chains in rubber, as reflected in the high elasticity of the latter.

The results of the experimental study which is described in the present paper and which is concerned with the x -ray diffraction spectra of amorphous rubber and of rubber which has become crystalline by stretching, lead to the conclusion that amorphous rubber contains fragments of molecular chains, the links of which do not scatter x -rays in the form of an amorphous ring. Furthermore, the experiments offer proof of the absolutely essential role of the above-mentioned molecular structure of rubber in determining a number of properties of the rubber.

In the x -ray diagrams of undeformed amorphous rubber, a single diffraction ring appears, the middle period of which, as is known, corresponds to the mean length of the van der Waals bonds. A diffraction spectrum of such nature is formed also by the interference of x -rays scattered by the links of adjacent molecular chains, which are united by van der Waals forces. The intensity of the amorphous ring obtained in this work indicates only the amount of the amorphous rubber in which the links of the chains are bound by intermolecular forces. This part of the amorphous rubber may be called the liquid part. During the stretching of raw natural rubber and certain types of synthetic rubber, and also their vulcanizates, there appear, besides the amorphous ring, interference spots, which as is already known, are attributable to crystallization of the rubber. The ratio of the intensity of the interference spots to the intensity of the amorphous ring in the diffraction spectrum is almost independent of the degree of stretching of the rubber, whereas the intensity of the crystalline interference increases with stretching. A quantitative investigation of the relative intensities of the amorphous ring and interference spots and the in-

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tensity of the interference line of a standard substance on the x-ray diagrams of stretched specimens of vulcanized rubber confirms this observation.

Figure 1 shows the results of measurements of the intensity of the amorphous ring as a function of the elongation for raw smoked-sheet rubber and two vulcanizates, NK-1 and NK-5. The composition of the NK-1 mixture was: smoked-sheet rubber 100, zinc oxide 5, stearic acid 2, sulfur 7, and mercaptobenzothiazole 3; that of the NK-5 mixture was: smoked-sheet rubber 100, zinc oxide 5, stearic acid 2, sulfur 2, and mercaptobenzothiazole 0.6. The experimental points on the curves correspond to the same final thickness of the specimens.

The constant intensity of the amorphous ring within a certain range of elongation which is clearly shown by the vulcanizates (at the lowest value of which the proportion of the crystalline phase reaches, according to our measure-

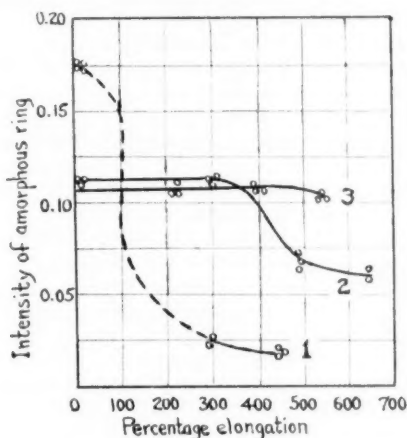


Fig. 1.—Intensity of the amorphous ring as a function of the degree of elongation.

1. Smoked-sheet rubber.
2. NK-5 vulcanizate containing 2 per cent sulfur.
3. NK-1 vulcanizate containing 7 per cent sulfur.

ments¹, 60 per cent) affords proof of the unchanged quantity of the liquid part of the amorphous substance in the process of crystallization. The independence of the intensity of the amorphous ring during stretching of vulcanizates of a given composition, with a simultaneously increasing intensity of crystalline interference, leads to the conclusion that the rubber crystals are formed, not from the liquid part of the amorphous substance, but from that part of it which gives no x-ray interference in the form of an amorphous ring. This part of the amorphous rubber, which crystallizes during stretching, and which we have termed the gaseous part, consists, according to our theory, of a combination of fragments of molecular chains. It should be noted also that a considerable change of density during crystallization accords with the theory proposed.

One might expect that the scattering of x-rays by the gaseous part of an amorphous rubber would be of the nature of gaseous scattering because of the small molecular regularity of this part of the substance. The gaseous part of amorphous rubber, from this viewpoint, is the factor which is responsible for its elastic properties.

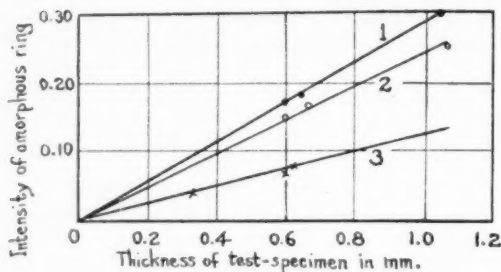


FIG. 2.—Intensity of amorphous rings.

1. Plasticized smoked-sheet rubber.
2. Unplasticized smoked-sheet rubber.
3. NK-31 vulcanizate.

It was of interest to compare the intensities of the amorphous rings of specimens of varying degrees of elasticity. Figure 2 shows measurements of the intensities of the amorphous rings of plasticized and unplasticized smoked-sheet rubber and of a highly elastic vulcanizate of NK-31 as a function of the thickness of the specimens (NK-31: 163 kg. per sq. cm.; relative elongation, 900 per cent; permanent elongation 14 per cent; creep under a weight of 20 kg. per sq. cm. for 50 hours, 5 per cent).

The specimen of plasticized smoked-sheet rubber, which had poor elasticity but which possessed plastic properties to a high degree, gave an amorphous ring of the greatest intensity. The least intense amorphous ring was observed for the vulcanizate of NK-31, which was highly elastic. The amorphous ring of unplasticized smoked-sheet rubber occupied an intermediate position.

It should be noted that ordinary smoked-sheet rubber, in addition to its elasticity, is characterized by a high degree of creep, which exceeds by 10 times the value of this same factor for vulcanized rubber.

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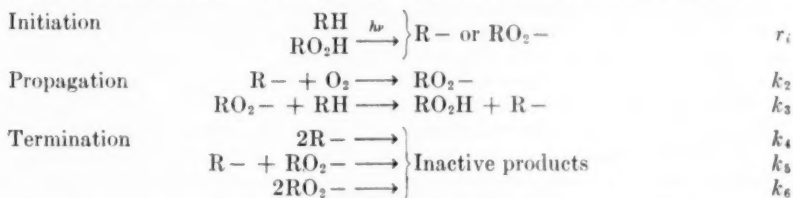
DETERMINATION OF ABSOLUTE RATE CONSTANTS FOR OLEFINIC OXIDATIONS BY MEASUREMENT OF PHOTOCHEMICAL PRE- AND AFTER-EFFECTS

I. AT "HIGH" OXYGEN PRESSURES *

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In an earlier publication¹ we reported an investigation which established that the photooxidation of two monoolefins (cyclohexene and 1-methylcyclohexene), a 1,4-diolefin (ethyl linoleate), and an isoprenic 1,5-diolefin (2,6-dimethylocta-2,6-diene)², in the approximate temperature range 0-30° C. proceeded in accordance with the following free radical chain mechanism³.



where RH represents the olefin, H an α -methylene hydrogen atom, r_i the rate of initiation ($= \phi_i I_a$, where ϕ_i is the primary quantum yield and I_a is the rate of light absorption), and the k 's are the velocity coefficients of the respective reactions. At oxygen pressures higher than about 50 mm., the stationary concentration of the R- radicals is so low that termination by reactions (4) and (5) is negligible, and the overall rate of oxidation is then given by:

$$r = k_3 k_6^{-1} [\text{RH}] r_i^{\frac{1}{2}} \quad (1)$$

The extinction coefficient and the efficiency of photolysis of RO_2H are so much greater than those of RH that the absorption of a small fraction of 1 per cent of oxygen is sufficient to render RO_2H virtually the sole initiating center.

A second paper⁴ described the application of the rotating sector technique to the separate determination of the propagation and termination constants in the pressure region where Equation (1) holds. Although the results appear to be quite satisfactory within the accuracy limits specified, the method lacks the facility and precision that it displays, for example, in certain polymerization reactions, for the following reasons. The essential experimental data are the ratios of the rates of oxidation in intermittent (\bar{r}) and constant (r_L) illumination as a function of the length of the light-dark cycle. The significant time range lies from 1 to 100 seconds; hence each measurement of \bar{r} , more especially for the longer periods, requires a considerable time (from about 0.3 to 2 hours). A

* Reprinted with certain omissions from the *Transactions of the Faraday Society*, Vol. 47, Part 2, pages 155-164, February 1951. A description of the experimental technique, a table giving experimental data on some of the substances examined, and three graphs of experimental results are omitted.

complete experiment thus occupies several hours and 1 per cent or more of oxygen is absorbed. Since the hydroperoxide produced catalyzes a thermal reaction in direct proportion to its concentration, a progressively increasing dark rate (r_D) is encountered, and which not only complicates the analysis of the results but intrinsically reduces their accuracy. To achieve the most favorable experimental circumstances necessitates a compromise in respect of temperature. If the latter is too high, the duration of the rate measurements is reduced, but the variations in r_D and the absolute magnitudes of r_D/r_L are much greater; if too low, the time factor becomes unduly large and uncertainties due to minor variations in light intensity, sector speeds, and the like can intrude. Despite these difficulties, the method retains its value, owing to its unambiguous interpretation, but an alternative requiring far fewer and less extensive rate measurements would clearly offer decided advantages.

In the second paper referred to, the relative values of k_3 and k_6 were noted to be such that on shutting off the light the transition from r_L to r_D should occupy a matter of minutes, and some consistent results were cursorily described (an ideally simple transition being considered). This paper reports accurate measurements and rigorous analysis of these photochemical after-effects (and pre-effects). The derived values of $k_3k_6^{-1}$ taken in conjunction with the corresponding $k_3k_6^{-1}$ ratios obtained via Equation (1) lead to separate evaluation of k_3 and k_6 . The required data for one determination are obtained in less time than a single point by the sector method, and a whole series of repetitive measurements can be made without any interference due to the increasing r_D . Experimentally, r_L and r_D have to be measured by a method sufficiently sensitive to define the transition between them, and other factors which inherently contribute to the pre- and after-effects actually found must be duly allowed for.

To afford a comparison with the sector results, dihydromyrcene and ethyl linoleate have been reinvestigated; we have also examined a Δ^1 -olefin (oct-1-ene), a tetraisoprene (2,6,11,15-tetramethylhexadeca-2,6:10,14-tetraene (digeranyl)), and the two natural long-chain polyisoprenes, gutta-percha and rubber.

Bamford and Dewar⁵ have recently applied a similar technique—which they had devised and used earlier in polymerization studies⁶—to the oxidizing tetralin system. In principle, the two approaches are equivalent, but our analysis of the experimental data is more direct, and we have formulated in detail the disturbances introduced by changes in rates of solution of oxygen and by delayed manometer response, since these greatly affect the accuracy of the derived $k_3k_6^{-1}$ values.

Theory of photochemical pre- and after-effects.—Consider a reaction proceeding at a steady rate r_L under constant illumination in the oxygen pressure region where Equation (1) holds.

At a time $t = 0$ the light is interrupted, and the rate falls progressively to the steady dark rate r_D . If r is the rate at an intermediate time t , the total reaction up to time t is $\int_0^t r dt$. Had the rate fallen abruptly to r_D at $t = 0$

the total reaction to time t would have been $\int_0^t r_D dt = r_D t$. We define the photochemical after-effect by the quantity:

$$I_d \equiv \int_0^t (r - r_D) dt \quad (2)$$

Experimentally this is evaluated by plotting the oxygen absorption as a function of t until the rate becomes constant, extrapolating back to $t = 0$, and reading off the intercept as shown in Figure 1.

The value of this intercept can be obtained from the kinetics of the process as follows.

If r_T is the thermal rate of chain initiation, the stationary dark rate r_D is given by:

$$r_D = k_3 k_6^{-1} [\text{RH}] r_T^{\frac{1}{2}} \quad (3)$$

and the overall rate at any instant by:

$$r = k_2 [\text{RH}] [\text{RO}_2 -] \quad (4)$$

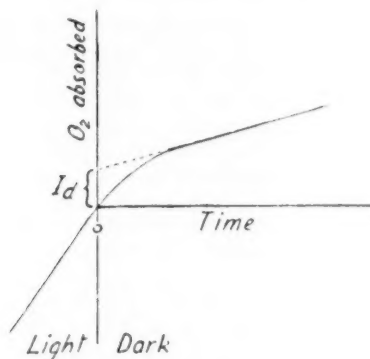


Fig. 1.—Definition of rate decay intercept, I_d .

Since $[\text{RH}]$ is essentially constant, the fall in r during the decay period arises from a fall in $[\text{RO}_2 -]$ and we have:

$$\frac{dr}{dt} = k_2 [\text{RH}] \frac{d[\text{RO}_2 -]}{dt} \quad (5)$$

Moreover, since $[\text{RO}_2 -]$ is controlled by the initiation and termination processes:

$$\frac{d[\text{RO}_2 -]}{dt} = r_T - k_6 [\text{RO}_2 -]^2 \quad (6)$$

Combining Equation (3) to (6) leads readily to the equation:

$$dr/dt = k_3^{-1} k_6 [\text{RH}]^{-1} (r^2 - r_D^2) \quad (7)$$

Then, from Equation (2):

$$I^r = \int_{r_L}^{r_D} \frac{r - r_D}{dr/dt} dr$$

whence

$$I_d = k_3 k_6^{-1} [\text{RH}] \ln \left(\frac{r_L r + r_D}{2 r_D} \right) \quad (8)$$

Measurements of r_L , r_D and I_d thus give at once a measure of $k_3 k_6^{-1}$.

The experiments may also be performed in the reverse direction by studying the rate growth after the light is switched on. In this case we obtain an intercept $I_0 \equiv \int_0^\infty (r_L - r)dt$. By a similar analysis:

$$I_0 = k'k_6^{-1}[\text{RH}] \ln \left(\frac{2r_L}{r_L + r_D} \right) \quad (9)$$

Disturbing factors.—(1) Rate of Solution.—In applying this method in practice, certain complications obtrude, of which the most serious arises from the finite rate of solution of oxygen. Experimentally, of course, we measure the rate of disappearance of oxygen from the gas phase, *i.e.*, the net rate of solution. In identifying this with the rate of reaction, two distinct difficulties have to be considered.

If the reaction has proceeded for sufficiently long to establish a steady (constant) rate, we can be sure that the oxygen concentration in the solution will be constant, and the net rate of solution then measures correctly the rate of oxidation. In general, however, the oxygen concentration will not be that (c_0) corresponding to saturation with respect to oxygen at the pressure of the gas phase, but some lower value (c). This discrepancy in concentration, Δc , depends on the efficiency of oxygen exchange between gas and solution, as we shall now formally demonstrate.

Assuming the solution to obey Henry's law, we may write for the rate of solution $k_s c_0$, where k_s is a constant depending on the shaking efficiency. Oxygen is lost from solution partly by reaction (rate r) and partly by evaporation (rate $k_e c$). The net rate of solution is thus $k_s(c_0 - c) = k_s \Delta c$, and in the steady state this must equal the rate of reaction r . Hence:

$$\Delta c = r/k_s \quad (10)$$

In the pressure range considered in this paper, the overall rate is independent of oxygen concentration, so no correction of r_L or r_D is needed on this account.

The second difficulty intrudes only when a reaction is studied in a nonsteady state. Under these circumstances, the net rate of solution is not necessarily equal to the rate of reaction, and the detailed reaction course cannot, therefore, be followed manometrically. This difficulty is reduced by our method of analyzing the data, since we use only overall measurements of the nonstationary period. All we need say therefore, at this stage, is that during this period the oxygen content of the solution will change: in passing from dark reaction to light reaction it is clear from Equation (10) that the concentration will decrease by $(r_L - r_D)/k_s$. Hence, if I_d' and I_0' are the intercepts found experimentally:

$$I_d' = I_d + (r_L - r_D)/k_s \quad (11)$$

$$I_0' = I_0 + (r_L - r_D)/k_s \quad (12)$$

By combining these two measurements, the solution correction is eliminated: subtracting (12) from (11) and substituting values of I_d and I_0 leads finally to the result:

$$I_d' - I_0' = k_s k_6^{-1}[\text{RH}] \ln \left\{ \frac{(r_L + r_D)^2}{4r_L r_D} \right\} \quad (13)$$

(2) Delayed Manometer Response.—Our experimental measurements of the nonstationary period were carried out at constant volume, using a differential octoil manometer to follow the associated pressure changes. These

changes are small compared with the total pressure, and they introduce no new complications in the correction for gas solubility, but the manometer suffers from the disadvantage of a delayed response. At any time when the manometer level is changing, its reaction is governed by the laws of viscous flow, and the driving force is the pressure differential across it, *i.e.*, the difference between the true oxygen pressure and the manometer reading. We are concerned only with manometer corrections in the stationary light and dark reaction zones, and it is easily seen that under stationary light conditions the error in the manometer reading is proportional to the rate r , *i.e.*, the problem is mathematically equivalent to the one previously discussed. The measured intercepts are therefore, each too large by a term of the form $(r_L - r_D)/k_m$, where k_m is a constant determined by the rate of manometer response. These corrections are additional, and similar in form, to those for oxygen solution. Moreover, they are automatically eliminated by taking the difference between the decay and growth intercepts. Equation (13) therefore represents our final result in the form in which we have applied it to the experimental data, and is believed to be free from spurious effects arising from the physical nature of the apparatus and procedure.

Estimated Rate of Solution.—When the ratio $k_3k_6^{-1}$ has been obtained from Equation (13), it can be used with Equation (8) to calculate I_d for comparison with the experimental quantity I_d' . We then have, allowing both for slow oxygen solution and slow manometer response:

$$I_d' - I_d = (r_L - r_D)(k_s^{-1} + k_m^{-1}) \quad (11')$$

k_m is readily determinable by subsidiary experiments in which the manometer is displaced from equilibrium and its time of free recovery observed: for the instrument used in our experiments $k_m^{-1} = 0.5$ second, which is in fact almost negligible compared with k_s^{-1} (~ 5 sec.).

TABLE II

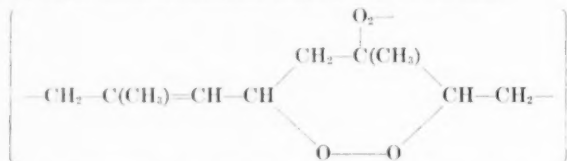
Olefin	Temp.	$10^4 k_3 k_6^{-1}$ (l. sec.^{-1}) ^a (mole^{-1})		$10^6 k_2 k_4^{-1}$ (mole^{-1}) ($\text{l.}^{-1} \text{sec.}^{-1}$) ^a		k_1 (mole^{-1} l. sec.^{-1}) ^a		$10^{-4} k_4$ (mole^{-1} l. sec.^{-1})	
						Present method	Sector method	Present method	Sector method
Oct-1-ene	25	0.53	0.1	0.03	—	0.03	—	0.3	—
	40	1.41	0.36	0.05 ₅	—	0.05 ₅	—	0.1 ₅	—
Cyclohexene	15	—	—	—	0.6 ₅	—	0.6 ₅	—	0.9 ₅
1-Methylcyclohexene	15	—	—	—	1.1	—	1.1	—	0.5 ₀
Dihydromyrcene	0	0.98	0.16	0.06	—	0.06	—	0.3 ₉	—
	15	—	—	—	0.2 ₀	—	0.2 ₀	—	0.6 ₅
	25	3.62	0.50	0.0 ₆	—	0.0 ₆	—	0.5 ₂	—
Digeranyl	25	10.7	2.0	0.5 ₅	—	0.5 ₅	—	0.2 ₅	—
	40	17.2	3.8	0.7 ₆	—	0.7 ₆	—	0.1 ₀	—
Gutta-percha	40	44.6	11	1.9	—	1.9	—	0.1 ₈	—
Rubber	25	24.8	3	2.1	—	2.1	—	0.6 ₈	—
	40	44.6	11	1.8	—	1.8	—	0.1 ₆	—
Ethyl linoleate	11	—	—	—	5.7	—	5.7	—	0.5 ₀
	25	121	22	6.6	—	6.6	—	0.3 ₀	—

^a Each propagation cycle in the 1,5-diolefins results in the incorporation of two oxygen molecules and, therefore, the values of $k_2 k_4^{-1}$ are one-half those calculated by the equations given in the text. The correction involved was overlooked in References nos. 1 and 4, but has now been applied to the k_1 value for dihydromyrcene quoted from the sector measurements.

DISCUSSION

Table II records the mean values of k_3 and k_6 now determined and the corresponding values determined by the sector method. The agreement between the comparative results is excellent, and offers convincing evidence of the equivalency of the two methods. It should perhaps be emphasized at this point that the absolute values of all the data quoted rest on the fundamental assumption that τ_T in benzoyl peroxide-catalyzed oxidations may be identified as one-half the rate of thermal decomposition of the peroxide at the same temperature. The basis for this assumption has been discussed by Bolland⁷ and by Bolland and ten Have⁸ and we believe it to be sound. However, Bamford and Dewar⁵ have recently questioned its validity and it must be admitted that uncertainty exists. A factor which would increase the values of k_3 and k_6 about three-fold is involved, and must be reckoned with in comparing the corresponding tetralin constants with those in Table II.

Two features of the results are noteworthy. First, the earlier conclusion⁴ that variations in $k_3k_6^{-1}$ (which measure relative oxidizabilities at constant τ_i) essentially reflect changes in k_3 is confirmed. All the k_6 values so far determined are practically the same, and comparison in this respect between oct-1-ene and ethyl linoleate is particularly striking. Furthermore in the case of the polyisoprenes, termination involves not allyl peroxido radicals as in the above two examples but cycloperoxide-substituted alkyl peroxido radicals⁹:



The accuracy of the constants determined at different temperatures is insufficient to yield significant values of the appropriate activation energies. However, the insensitivity of k_6 to wide structural differences, its small and irregular changes with temperature, and the more consistent changes shown by k_3 (especially in dihydromyrcene), strongly suggest that almost the whole of the activation energy associated with $k_3k_6^{-1}$ must be attributed to k_3 .

Secondly, the increase in oxidizability at constant rate of initiation on ascending the polyisoprene series, as expressed in the $k_3k_6^{-1}$ values, is evidently to be associated with changes in k_3 . The alternative possibility that the termination process is hindered in the more viscous solutions of the high polymers, just as occurs in certain polymerization systems, *i.e.*, the gel effect¹⁰, may, therefore, be discounted for our experimental conditions.

REFERENCES

- ¹ Bateman and Gee, *Proc. Roy. Soc. (London)* **A195**, 376 (1948).
- ² Hereafter described as dihydromyrcene.
- ³ Contemporaneously other work in these laboratories revealed that, for dihydromyrcene, four rather than two reactions comprise the propagation cycle (*cf.* Bolland and ten Have, *Trans. Faraday Soc.* **45**, 93 (1949); Bolland and (Mrs.) Hughes, *J. Chem. Soc.* **1949**, p. 492). Since the additional reactions simulate Reaction (2) in being very fast compared with Reaction (3), the kinetic relationships demanded by the foregoing scheme are still obeyed.
- ⁴ Bateman and Gee, *Proc. Roy. Soc. (London)* **A195**, 391 (1948).
- ⁵ Bamford and Dewar, *Proc. Roy. Soc. (London)* **A198**, 252 (1949).
- ⁶ Bamford and Dewar, *Proc. Roy. Soc. (London)* **A192**, 309 (1948).
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- ⁸ Bolland and ten Have, *Trans. Faraday Soc.* **45**, 201 (1947).
- ⁹ Bolland and ten Have, *Trans. Faraday Soc.* **45**, 93 (1949); Bolland and (Mrs.) Hughes, *J. Chem. Soc.* **1949**, p. 492.
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OXIDATION OF OLEFINS REPRESENTING SOME STRUCTURAL UNITS OF GR-S*

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In recent years there has been increasing interest in the oxidation of rubber, petroleum, drying oils, and related materials, because these groups of organic compounds represent vast industries in which oxidation is a vitally important factor. Recent reviews on the subjects of oxidation of elastomers¹, lubricating oils², drying oils³, and more specifically olefins⁴, indicate both the difficulty and the importance of ultimately obtaining a more thorough understanding of the fundamental mechanisms involved. The complexity of the problem is enhanced by the large number of variables encountered, which include physical state, catalysis (homogeneous or heterogeneous), activation (thermal or photochemical), structure (polymers or compounds of low molecular weight), and oxidizing agents (including oxygen and ozone).

The kinetics have been studied extensively and the most fundamentally satisfactory theory at present is that of Bolland and coworkers⁴, involving a free radical mechanism. Chemically, oxidations are generally considered to proceed through the formation of a hydroperoxide group, which in the case of olefins is postulated at the α -methylenic position⁵. This theory has been recently revised to the extent that for unsaturated fatty acids the initial attack is thought to be on the double bond for a very few molecules, which results in α -methylenic hydroperoxide formation for many molecules by a biradical mechanism³. Other workers have indicated that initial attack on the double bond is likely⁶.

The purpose of the present work was to study the kinetics and chemistry of the oxidation of three olefins which are structurally related to GR-S—namely, 1-phenyl-4-hexene, 1-phenyl-3-pentene, and 2-octene. The phenyl derivatives represent structures formed by the union of butadiene and styrene, while the octene represents an isolated olefin group such as would be present in a polybutadiene segment of the polymer chain. This study is confined to liquid phase, autocatalytic, thermally activated oxidation with molecular oxygen. It is hoped that the information thus obtained will contribute to the ultimate determination of the mechanism for oxidative degradation of both natural and synthetic rubber.

EXPERIMENTAL PROCEDURE

Materials.—1-Phenyl-3-pentene and 1-phenyl-4-hexene were prepared by the method of Lawrence and Shelton⁷. All olefins, except the first preparation of phenylpentene, were purified by fractionation through a 36-inch helix-packed, electrically heated column and analyzed for purity by a bromate-bromide volumetric method. The first preparation of phenylpentene, purified by distillation only, boiled at 84.5° to 87.5° C at 10 to 12 mm. of mercury, with

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a purity of 79.2 per cent. The second preparation boiled at 84.5° to 85.0° C at 13 to 14 mm. of mercury, and analyzed 97.9 per cent. The phenylhexene boiled at 86.0° to 89.0° C at 8 mm. of mercury, and analyzed 100.4 per cent. The position of the double bond for each had been established by Lawrence and Shelton⁷. Refractive index and density determinations on the high purity preparations checked well with those of the literature. All boiling points were stem-corrected.

The 2-octene was obtained through the courtesy of the Lubrizol Corp., Cleveland, Ohio. The fractionated material boiled at 124.0° to 126.5° C at 745 mm. of mercury and analyzed 95.3 per cent pure. The observed refractive index and density checked closely with literature values for 2-octene but not for 1-octene.

Apparatus.—The apparatus was essentially the same as that used by Lawrence and Shelton⁷, who describe the oxygen flow and absorption bulbs. The only differences were that here a dual system of two absorption trains (Figure 1) was used, enabling duplicate runs to be made simultaneously, and capillary tubes were sealed to the bottom of the absorption bulbs and extended up along the sides, ending in stopcocks and U-tubes to allow sampling during runs. The volumes of trains 1 and 2 (right and left, respectively, in Figure 1) exposed to variation in room temperature were determined from the ideal gas law by finding the slope graphically on a plot of the buret reading *vs.* reciprocal of pressure for five pressures. The volumes exposed to temperature variation after subtracting the volumes of the absorption bulbs and condensers were 360 ± 5 cc., which excluded the buret reading. Temperature of oxidations was known to 0.1° C, and was held to $\pm 0.25^\circ$ C with a Fenwall No. 17510 controller.

Procedure.—The procedure in preparation for making runs was to install fresh Drierite and Ascarite in the Nesbitt tubes for removing water and carbon dioxide. Leak tests of a day or more were made to ensure tightness. Pumping rate tests were made and the rate was set at approximately 45 cc. per minute. The olefin samples of 20 or 25 cc. were pipetted in, the system was sealed, initial buret readings were made, and pumps were started. Readings were made by bringing the systems to 760-mm. pressure with a head of the concentrated sodium acetate solution used as the confining liquid. Although this solution has a very small vapor pressure, the oxygen from the buret was passed through a U-tube of Drierite before it entered the system to ensure absence of water vapor. Temperature corrections were then applied to the buret reading plus 360 cc. to obtain the true volume at a standard reference temperature of 25° C. The buret was refilled with oxygen as required and samples were removed periodically for determination of peroxide and olefin. At the end, the remaining olefin was emptied by pressure through the sampling tube and a short leak test was made. Pumping rates were then tested and the absorption trains were dismantled, so the last portions of oxidized olefin could be removed from the bulbs.

Material balances were made on 16 runs in which olefin and oxygen put in were balanced against oxidized olefin, water, and carbon dioxide removed. The average error was 2.3 per cent.

Analyses.—The peroxide method of Wagner, Smith, and Peters⁸ was modified by using one-fifth of their quantities. Accuracy was within 2 per cent, based on pure crystalline benzoyl peroxide. Only a small blank was necessary. Reproducibility was ± 0.02 per cent for the peroxidic oxygen present, which varied from 0 to 5 per cent on a series of sixteen analyses made in duplicate on two runs with 2-octene. The authors⁸ gave ample evidence that there is no interference by olefins.

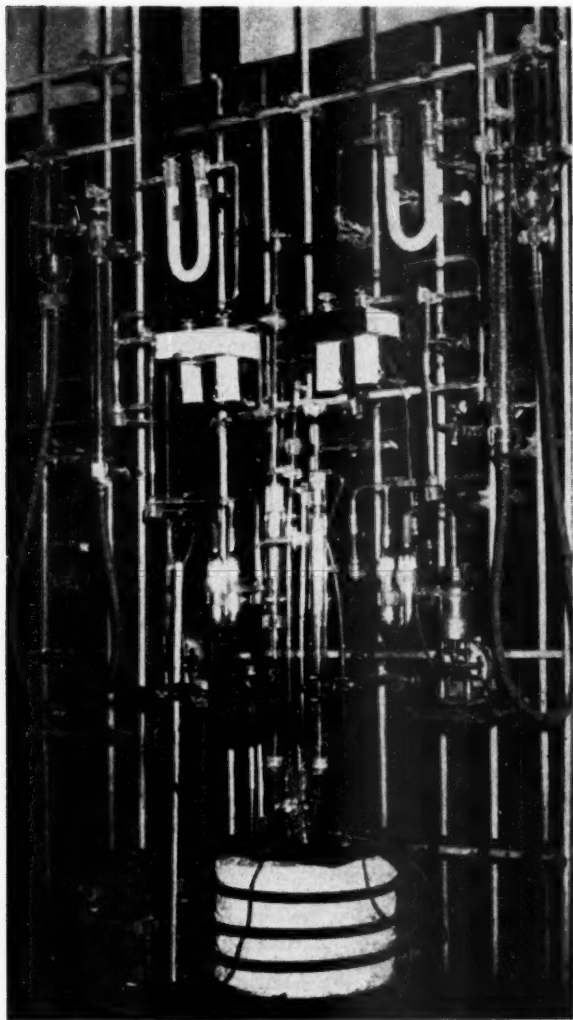


FIG. 1.—Oxidation apparatus showing dual absorption trains.

A potassium bromide-bromate determination of olefins was employed, which was accurate to within 1 per cent based on pure styrene and reproducible to ± 1 per cent based on octene runs. As *tert*-butyl hydroperoxide caused no effect on the end point and benzoyl peroxide only a small effect, no corrections for the presence of peroxides were necessary.

The acid content was determined by titration to the phenolphthalein end point with approximately 0.05 *N* alcoholic potassium hydroxide. The ester content was determined by back-titration with 0.05 *N* aqueous hydrochloric

acid after 1 hour of refluxing in the presence of excess caustic. The method of Siggia⁸ adapted from that of Bryant and Smith was employed for carbonyl oxygen, which uses standard alcoholic potassium hydroxide for titration of the hydrochloric acid liberated from hydroxylamine hydrochloride.

ABSORPTION DATA AND CALCULATIONS

The oxygen absorption data were all converted to moles of oxygen per mole of original olefin. Because it was necessary to correct constantly for the amount of sample removed, the following formula was used:

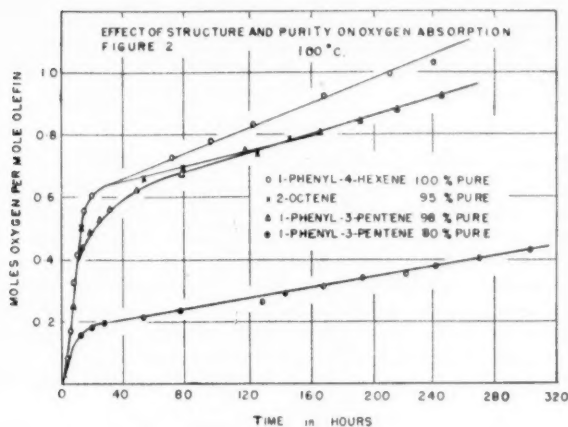
$$M = \frac{\frac{\text{cc. O}_2}{24,440 \text{ cc./mole}}}{\text{moles of original olefin} \left(\frac{\text{grams of original olefin} - \text{removals}}{\text{grams of original olefin}} \right)}$$

where M = moles of oxygen per mole of original olefin. The limitation of the accuracy of this correction is the assumption that the weight of carbon and hydrogen removed to carbon dioxide and water, respectively, at any time is compensated by the weight of oxygen absorbed into the liquid. This assumption is correct to within an average of 10 per cent at the ends of sixteen runs and probably holds well within this range at shorter times. The resulting effect on the value of M is, of course, very much less.

It was found that pumping rate did not affect the oxygen absorption curves in the range of 30 to 60 cc. per minute. This was at all times greater by a factor of 10 or more than the fastest instantaneous absorption rate. However, sampling had the effect of increasing absorption rate, even to the extent that the sampled runs usually absorbed more total cc. of oxygen than their unsampled partners which originally contained equal weights of the same olefin. This effect was not due to differences in the two trains, because it was observed on both. Runs in which both trains were sampled agreed closely, but unsampled runs did not correlate well with each other, or vary in a regular manner with temperature. The explanation probably lies in the factor of viscosity, and the breaking up of channels by sampling. This idea is strengthened by the fact that at the lowest temperature studied the difference between sampled and unsampled runs was the greatest. Channeling in the unsampled system results in a decrease in the effective surface for diffusion of oxygen from the gas to the liquid phase. It would seem reasonable that the gas diffusion rate would depend on the surface area between the liquid and gas phases. This factor is not so apparent in the early stages, but it becomes more important as oxidation progresses and the material becomes more viscous.

EFFECT OF STRUCTURE AND PURITY

The variation of oxygen absorption with time for the three olefins is shown in Figure 2. The fourth curve is for 1-phenyl-3-pentene at low purity. Apart from the induction period, the two commonly recognizable stages are evident. These consist of (1) the autocatalytic stage in which peroxides are present in quantity and (2) the constant-rate stage involving largely the formation of secondary products. The rates of oxidation in these two stages offer means for comparing different structures for relative ease of oxidation. Table I lists the rate at the point of inflection, which is a measure of autocatalytic reactivity, and the linear rate, which is a measure of the reactivity in the later constant-rate stage.



It can be seen that the low-purity phenylpentene oxidized much more slowly than the high-purity material in both stages. Confining all attention to 100°C momentarily, it can be seen that phenylhexene is the most reactive olefin studied. 2-Octene equals it in the autocatalytic stage but not in the constant-rate stage. Phenylpentene shows a lower reactivity in the autocatalytic stage than either the octene or phenylhexene, but exceeds octene in the linear portion. These conclusions are consistent qualitatively with previous comparisons⁷, where the high reactivity of phenylhexene has been attributed to the possibility of activation of oxygen attack at two points separated by a methylene group, one activated by the phenyl group and the other by the double bond. In phenylpentene, the two activated points are adjacent and hence thought to interfere, thus causing lower oxidizability. Present data indicate that, in the autocatalytic stage, the presence of the phenyl group activates in phenylhexene but interferes in phenylpentene, since the aliphatic compound is intermediate

TABLE I
RELATIVE REACTIVITIES OF THREE OLEFINS
1-Phenyl-4-hexene

Temp. (°C)	Purity ^a (%)	Run (hours)	Point of Inflection		Linear rate × 1000 =
			Hours	Rate	
99.9	100.4	241	6.6	0.055	1.96
89.8	100.4	260	15.0	0.033	2.36
89.8	100.4	260	17.0	0.037	2.30
80.1	100.4	264	44.0	0.014	2.92
1-Phenyl-3-pentene					
100.0	79.2	341	7.2	0.024	0.84
100.0	97.9	247	6.5	0.046	1.51
90.0	97.9	237	10.5	0.028	1.39
2-Octene					
100.0	95.3	193	11.0	0.060	1.20
100.0	94.3	45	9.0	0.049	1.42
				Av. 0.055	1.31

^a Based on experimental determination of unsaturation.

in autocatalytic reactivity. A casual glance at Figure 2 reveals that at comparable purity the curves are similar and, hence, that they probably all proceed by the same fundamental mechanism and that the double bond is involved either directly or indirectly.

EFFECT OF TEMPERATURE

Absorption curves of 1-phenyl-4-hexene at three temperatures are plotted in Figure 3. It will be noted that the autocatalytic rate is greater, the higher the temperature. However, the time to the break point, the total absorption, and the linear rate all vary inversely with temperature. The former would be expected, but the latter two factors must be involved in the mechanism of the linear stage, which includes the formation of secondary oxidation products. At the lower temperatures, oxidation apparently proceeds more closely to the maximum possible in this later stage, either because volatile intermediate or end products exert an effect and remain longer or because of a changing ratio of oxidation reactions to others which require no oxygen—esterification, for example.

Table I reveals essentially the same results as Figure 3, except that the linear rates for phenylpentene are close together for the two temperatures studied. Thus it can be concluded that the rate at the point of inflection is ap-

TABLE II
OXYGEN ABSORPTION DATA

Hours	Moles O ₂ per mole original olefin, <i>M</i>	Instantane- ous rate <i>R</i> × 100	Molar concentrations		Overall rate constant <i>k</i> × 100
			Unreacted olefin	Pero- xide	
A. 1-Phenyl-4-hexene, 80.1° C					
0	0	—	5.17	0.02	—
5.0	0.016	0.440	5.02	0.12	0.73
11.0	0.050	0.73	4.74	0.32	0.48
18.0	0.108	0.99	4.31	0.55	0.42
24.0	0.173	1.18	3.84	0.79	0.39
30.0	0.252	1.30	3.36	1.00	0.39
44.0	0.429	1.38	2.36	1.31	0.45
54.5	0.584	1.31	1.82	1.41	0.51
68.0	0.732	1.19	1.31	1.32	0.69
76.3	0.831	1.12	1.07	1.25	0.84
125.3	1.218	0.440	0.60	0.69	1.06
196.9	1.431	0.292	0.60	0.32	1.52
264.0	1.631	0.292	0.60	0.24	2.02
Average to underlined value					0.55
B. 1-Phenyl-4-hexene, 89.8° C					
0	0	—	5.14	0.02	—
6.0	0.077	1.90	4.44	0.42	1.02
12.0	0.224	3.10	3.39	0.90	1.01
18.6	0.421	3.20	2.06	1.12	1.39
24.0	0.580	2.74	1.51	1.15	1.58
31.0	0.744	1.96	1.32	0.94	1.58
50.5	0.962	0.76	1.26	0.42	1.44
68.8	1.040	0.35	1.25	0.24	1.17
98.5	1.116	0.236	1.16	0.17	1.20
120.0	1.178	0.236	1.10	0.14	1.53
213.5	1.374	0.236	0.95	0.14	1.78
259.5	1.492	0.236	0.87	0.14	1.94
Average to underlined value					1.33

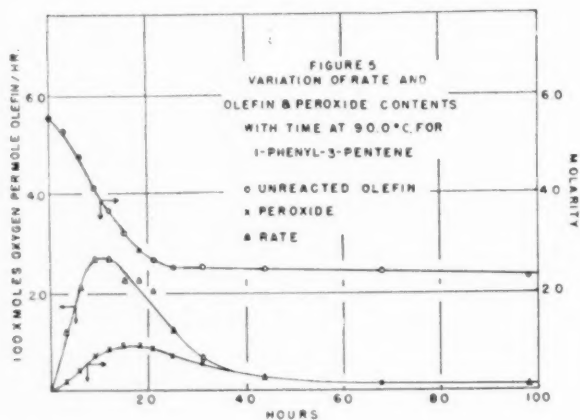
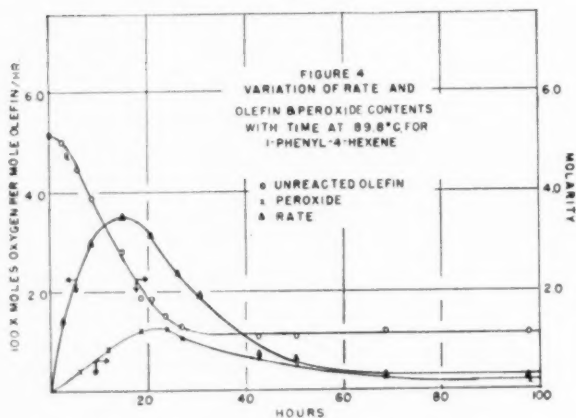
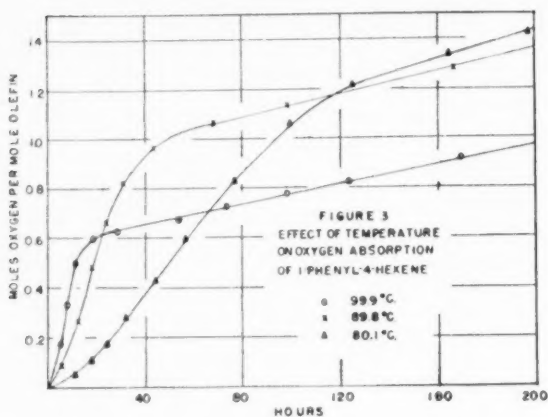
TABLE II—Continued

Hours	Moles O ₂ per mole original olefin, <i>M</i>	Instantane- ous rate <i>R</i> × 100	Molar concentrations		Overall rate constant <i>k</i> × 100
			Unreacted olefin	Pero- xide	
C. 1-Phenyl-4-hexene, 89.8° C					
0	0	—	5.14	0.02	—
6.0	0.090	2.10	4.45	0.41	1.15
12.0	0.263	3.45	3.35	0.88	1.17
18.6	0.483	3.43	2.00	1.20	1.43
24.0	0.654	2.81	1.49	1.26	1.50
27.0	0.735	2.48	1.27	1.21	1.61
43.0	0.964	0.84	1.11	0.51	1.48
68.8	1.069	0.230	1.10	0.18	1.16
98.5	1.140	0.230	1.09	0.17	1.24
120.0	1.200	0.230	1.06	0.14	1.55
213.5	1.384	0.230	0.97	0.14	1.70
259.5	1.525	0.230	0.89	0.14	1.85
Average to underlined value					1.37
D. 1-Phenyl-3-pentene, 90.0° C					
0	0	—	5.52	0.04	—
6.0	0.076	2.10	4.73	0.42	1.06
12.0	0.229	2.69	3.64	0.88	0.84
18.0	0.383	2.07	2.84	0.92	0.79
25.0	0.501	1.21	2.52	0.70	0.69
31.0	0.559	0.66	2.50	0.54	0.49
44.0	0.615	0.30	2.45	0.28	0.44
98.0	0.738	0.106	2.35	0.17	0.27
163.0	0.803	0.106	2.24	0.085	0.56
189.5	0.839	0.106	2.18	0.085	0.57
216.7	0.877	0.106	2.12	0.085	0.59
237.0	0.910	0.106	2.09	0.085	0.60
Average to underlined value					0.63
E. 1-Phenyl-3-pentene, 100° C					
0	0	—	5.49	0	0
6.5	0.219	4.54	3.72	0.84	1.45
12.5	0.419	1.77	2.89	0.59	1.04
18.5	0.480	0.89	2.83	0.28	1.13
24.5	0.529	0.60	2.81	0.16	1.33
30.5	0.569	0.49	2.79	0.11	1.60
49.0	0.621	0.24	2.73	0.068	1.29
79.5	0.683	0.151	2.63	0.063	0.91
119.0	0.751	0.151	2.51	0.057	1.05
168.0	0.811	0.151	2.35	0.049	1.31
218.5	0.860	0.151	2.19	0.042	1.64
246.5	0.926	0.151	2.09	0.039	1.85
Average to underlined value					1.33

parently a better criterion for comparing structures because (1) it measures the autocatalytic stage where the initial reactivity of the olefin is predominant, (2) it varies normally with temperature, and (3) viscosity is lower than at later stages, which means better reproducibility.

PEROXIDE AND OLEFIN CONTENT

Peroxide and olefin analyses were made during the oxidation runs because they are intimately related to both the kinetic and chemical mechanisms. Table II lists these and instantaneous rate data, all of which were obtained graphically



from enlarged plots of the type shown in Figures 4 and 5. The points of these plots indicate the order of experimental variability. It was found desirable to convert to a molar basis to have a familiar and common basis upon which to consider the kinetic relationships. Densities were determined at elevated temperatures and were 0.831 and 0.25 gram per cc. at 80° and 90° C, respectively, for 1-phenyl-4-hexene and 0.830 and 0.819 at 90° and 100° C, respectively, for 1-phenyl-3-pentene. The formulas used for conversion of the original analytical results expressed as percentage concentrations of peroxide and of olefin to molar concentrations were as follows:

$$\text{Molar concentration of olefin peroxide} = \frac{(\% \text{ peroxidic O}_2)(10)(\text{density})}{(\text{mol. wt. O}_2)}$$

$$\begin{aligned} \text{Molar concentration of unreacted olefin} \\ = \frac{(\% \text{ unreacted olefin})(10)(\text{density})}{(\text{mol. wt. of olefin})} \\ - \text{molar concentration of olefin peroxide} \end{aligned}$$

The latter correction must be made because in all probability the peroxide is largely hydroperoxide, at least initially, and hence would analyze as both olefin and peroxide.

The molar concentrations of unreacted olefin and peroxide, and instantaneous rates, are plotted in Figures 4 and 5 for phenylhexene and phenylpentene at 90° C. The rate rises rapidly at the start, accompanied by a rapid drop in unreacted olefin content. The peroxide content rises to a maximum after the rate maximum and shortly thereafter almost equals the unreacted olefin content in the case of phenylhexene. The peroxide and rate curves ultimately level off at an essentially constant value. The olefin curve also becomes linear, but with a small downward slope. It will be noted from Table II that the peroxide content is higher at lower temperatures, a fact that was also observed by Tobolsky, Metz, and Mesrobian¹⁰.

DIFFERENTIAL RATE EQUATION

A satisfactory kinetic mechanism must relate quantitatively the factors just discussed. This is the purpose of the reaction rate constant, k , shown in Table II, the values of which were found from the differential equation:

$$\text{Rate, } dM/dt \text{ (hours)} = k (\text{unreacted olefin})(\text{olefin peroxide})$$

where M equals moles of oxygen per mole of original olefin and the parentheses represent molar concentration. This equation is consistent with the kinetic results reviewed by Bolland⁴ and Robertson¹¹. Oxygen concentration was constant in this study and consequently does not appear as a variable in the above equation. The constant ordinarily holds through the autocatalytic stage and in the case of phenylpentene through the whole time. The k values were averaged up to the point where the deviation became excessive, as indicated by the line which separates the values included in the average from the rest of the data in the appropriate column of Table II. The reason for the deviation is probably related to the formation of a diperoxide¹² or by direct attack at the double bond to form a peroxide. If these reactions occur, they would cause a decrease in unsaturation and the high observed value of the constant near the

end would result, as the assumption that all peroxides are olefin hydroperoxides would not be completely valid. Thus in subtracting the total peroxide concentration from the total olefin concentration, the calculated molar concentration of the unreacted olefin would be too low and the constant correspondingly high. Also, the diperoxide might be less reactive and less likely to be quantitatively determined by the iodometric method employed⁸.

A pertinent check on the validity of the premise that the average rate constants determined in Table II represent a rate-determining chemical reaction can be made by determining energies of activation by the Arrhenius equation:

$$2.303 \log \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{R(T_2 T_1)}$$

where E = energy of activation, calories per mole

R = 1.987 calories per mole degree

T_2, T_1 = temperature in °K

k_2, k_1 = reaction rate constants at T_2 and T_1 , respectively.

For 1-phenyl-4-hexene between 80.1° and 89.8° C, the constants of 0.0055 and 0.0135 (average of values in Table II, parts B and C) give 23,500 calories per mole activation energy. For 1-phenyl-3-pentene between 90.0° and 100.0° C, the constants of 0.0063 and 0.0133, respectively, give 20,100 calories per mole for E . These are in the range normally encountered for true chemical reactions and hence add support to the validity of the preceding treatment.

PROBABLE CHEMICAL MECHANISM

In an effort to determine the chemical mechanism, determinations of functional groups containing oxygen were made—namely, acid, ester, and carbonyl. The analyses made accounted for the majority of the oxygen, which is consistent with results of other workers¹³. Other products which have been reported are epoxides, ethers, and alcohols, but these have usually been in the minority or absent². High free-alcohol content¹⁴ seems to occur only when opportunity for esterification is absent. The high water and carbon dioxide percentages observed at the completion of the runs are consistent with the fact that oxidation was prolonged. The peroxide content at the end represents the steady-state concentration and is only a minor part of the oxygen at high stages of oxidation. The carbonyl analyses probably represent ketones, since aldehydes would be expected to oxidize under the conditions involved.

There is little doubt that a hydroperoxide (probably α -methylene) is one of the most important initial molecular intermediates of oxidation of an olefin¹⁵. Hydroperoxides are known to be reactive compounds and to be capable of initiating reactions which can form the functional groups usually observed. Lawrence and Shelton⁷ isolated phenyl 1-propenyl ketone and benzoic acid from the oxidation of 1-phenyl-2-butene and proposed a molecular mechanism based on hydroperoxide reactivity, which is probably applicable to the olefins of this study.

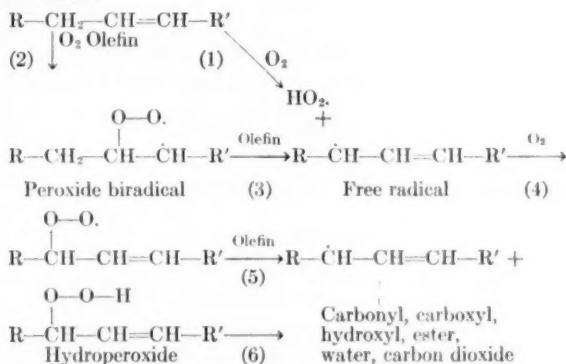
The subsequent mechanism postulates that initiation may involve either an α -methylene attack or a peroxide biradical of a type originally postulated by Farmer¹⁶, which could be formed by direct attack at the double bond and which would be capable of initiating a free radical chain mechanism of the type proposed by Bolland⁴ and others¹⁷.

Main Reactions:

1. Formation of free radicals by oxygen attack at α -methylene group.
2. Formation of a peroxide biradical by attack at the double bond.
3. Formation of free radicals by attack of the biradical on an olefin.
4. Reaction of the α -methylene free radicals with oxygen.
5. Chain-propagating, rate-determining, autocatalytic reaction for which the above differential rate equation applies.
6. Formation of observed ultimate functional groups and simple molecules from the hydroperoxide by way of reactions which have been thoroughly discussed in the literature¹⁸ but which are probably subsequent to the rate-determining reaction.

Thus the significant information which has been obtained from chemical and kinetic data in this study and from the extensive literature in the field has been correlated into a single plausible scheme based on the postulate that initial attack at the double bond plays an important role, even though the major reaction appears to involve attack at the α -methylene group. Reaction 5 involving olefin and peroxide is the one that correlates with the differential rate equation and the kinetic mechanism of Bolland⁴. Further work aimed toward the ultimate goal of a more complete understanding of the oxidation of both simple olefins and more complex systems such as natural and synthetic rubber is in progress.

Main Reactions:



CONCLUSIONS

Although all three olefins oxidized have essentially the same oxidation curves, the phenyl group was found to activate the autocatalytic rate of oxidation when separated from the point of unsaturation by three methylene groups and to hinder the autocatalytic rate when separated by only two methylenic groups as compared to an unsubstituted olefin.

Increasing temperature increases the autocatalytic absorption rate but decreases the rate in the subsequent linear state of absorption.

Increasing temperature lowers peroxide concentrations, both at the maxima and in the steady states.

The differential rate equation relating the variable concentrations is:

$$\text{Rate, } \frac{dM}{dt} = k (\text{unreacted olefin})(\text{peroxide})$$

A general chemical mechanism has been postulated which is based upon attack at both the α -methylene group and the double bond, with the formation in the latter case of a peroxide biradical capable of initiating a chain reaction mechanism. The reaction between olefin molecules and α -methylenic peroxide radicals is proposed as the rate-determining step.

Similar chemical and kinetic mechanisms are probably involved in the oxidation of more complex organic olefinic structures such as are present in natural and synthetic rubber. Other factors, including the effect of compounding ingredients, serve to complicate the picture in such materials.

SUMMARY

Three olefins were oxidized in the liquid phase with molecular oxygen to determine the kinetics of the oxidation reactions and the relationship to oxidation of rubber.

The instantaneous rate of oxidation was found to be related to the analytically determined olefin and peroxide concentrations by the equation: Rate = k (unreacted olefin)(peroxide), where rate equals moles of oxygen per mole of original olefin per hour and the parentheses represent molarities. Presence of a phenyl group was found to affect k , but only in a minor way, indicating that the same fundamental kinetic mechanism applies in both aromatic and aliphatic olefins.

The data are consistent with the general kinetic mechanism of Bolland involving oxygen attack at the α -methylenic group. However, it appears probable that initial oxygen attack can also occur at the double bond, resulting in the formation of a peroxide biradical, which may then react with other olefin molecules, initiating the usual chain reaction mechanism.

ACKNOWLEDGMENT

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THE NATURE OF STRUCTURAL CHANGES OF BUTADIENE RUBBERS CAUSED BY HIGH TEMPERATURES (100–200° C) *

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In theories developed by Kuzminskiĭ and his collaborators¹ concerning the mechanism of oxidation of rubbers, the question of a direct thermal effect on their structure was not discussed. Nevertheless, with certain rubbers, structural changes which are caused by high temperatures play a very important part in the total complex of structural changes undergone by these rubbers during processing and, after vulcanization, by their products during service.

Dogadkin², Zayonchkovskiĭ, Zayonchkovskaya, Pisarenko, and Astafyez³, Kuzminskiĭ, Shanin, Degteva, Lapteva⁴, and other Soviet investigators have shown that, when butadiene rubbers are heated in the temperature range of 100–200° C, structural changes take place which are characterized by increases of tensile strength and modulus, decrease of extensibility, decrease of unsaturation, etc. The question of the causes of such extensive changes in rubber is the subject of this discussion.

Rebinder has proven unsubstantiated the reasoning of several investigators regarding these processes, and has shown the necessity of carrying out direct experiments which would provide an explanation of their nature.

This problem, then, boils down to whether the structural changes are a result of the formation of activated oxygen or are the direct effect of high temperatures on the structure of rubbers, and any difficulties involved arise from lack of a method of detecting and eliminating small quantities of oxygen which are inevitably present in rubber, even after evacuation in a high vacuum and during treatment in an atmosphere of nitrogen.

The method elaborated by the authors and described in the present paper makes it possible to study the thermal changes of rubbers in the complete absence of free oxygen.

It is clear from Figure 1 that the heating of butadiene rubbers in a high vacuum at 200° C causes a great decrease of unsaturation in the side chains of their molecules. The greater the number of double bonds in the original rubber, the faster are they eliminated in this process. This change of saturation in the main chains takes place only at the beginning of the thermal treatment.

In a separate series of experiments the kinetics of consumption of the inhibitor (in this case phenyl- β -naphthylamine) when rubber was heated in an atmosphere of nitrogen was studied. The measurements are given in Figure 2.

Consumption of the inhibitor is observed only during the initial stage of the process; after further heating the inhibitor does not enter into the reaction.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Reports of the Academy of Sciences, USSR*, Vol. 74, No. 4, pages 725–727, Oct. 1, 1950.

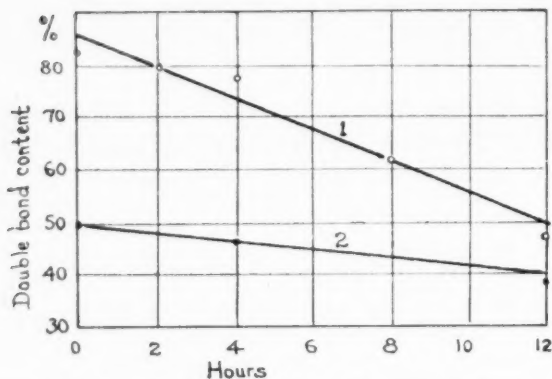


Fig. 1.—Change of double bond content in side chains of vulcanized butadiene rubbers during heating in a high vacuum at 200° C.

1. Rubber containing 83% double bonds in the side chains.
2. Rubber containing 50% double bonds in the side chains.

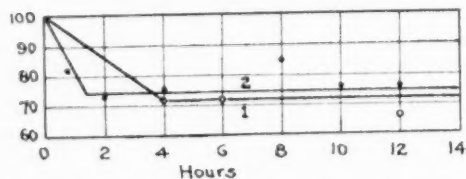


Fig. 2.—Kinetics of consumption of inhibitor in butadiene rubber during heating in an atmosphere of nitrogen. The double bond content in the side chains of the rubber was 83 per cent.

1. Temperature, 120° C.
2. Temperature, 200° C.

We may suppose that the initial consumption of the inhibitor is caused by its reaction with the more active double bonds of the main chains of the rubber. In this case the altered ratio of double bonds of the main chains to those of the

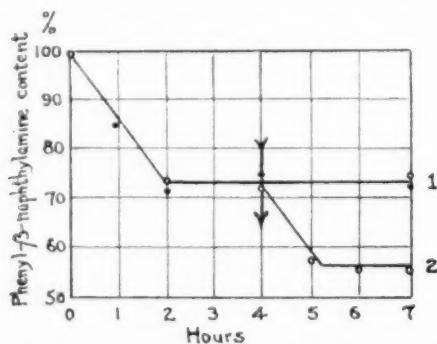


Fig. 3.—Kinetics of consumption of inhibitor during heating of butadiene rubbers in an atmosphere of nitrogen at 200° C.

- For rubber containing 17% double bonds in main chains.
- For rubber with 50% double bonds in main chains.
- (1) Consumption of inhibitor in experiments without addition of oxygen.
- (2) Subsequent additional consumption of inhibitor after addition of oxygen.

side chains would cause a change of the shape of the curve of consumption of inhibitor. However, it is clear from Figure 3 that the consumption of inhibitor in the two rubbers, which differ in the position of double bonds in their molecules, is represented by the same curve. Consequently, the consumption of inhibitor can bear no relation to the differing activity of the various elements in the structure of the rubbers. We are, therefore, led to the conclusion that the consumption is caused by the presence of traces of oxygen in the rubber.

To verify this assumption, the following experiment was performed. A short time after the initial consumption of the inhibitor ceased (at the point on the curve marked by an arrow in Figure 3), a measured quantity of oxygen was added to the system. This resulted in a renewed consumption of inhibitor until all the oxygen had reacted. This phenomenon repeated itself every time that a new quantity of oxygen was added to the system, and it is of great significance for an understanding of the mechanism of the action of the inhibitor.

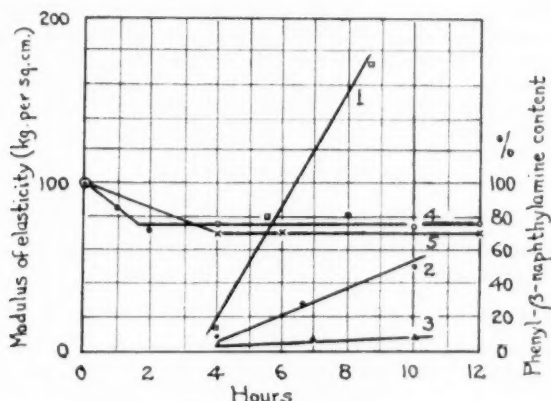


Fig. 4.—Change of modulus of elasticity of butadiene rubber during heating in complete absence of free oxygen.

1. Change of modulus at 200° C.
2. Change of modulus at 170° C.
3. Change of modulus at 150° C.
4. Kinetics of consumption of inhibitor at 200° C.
5. Kinetics of consumption of inhibitor at 120° C.

Of no less importance in the study of rubbers is the possibility thereby offered of establishing the kinetic limits of the process when free oxygen is altogether absent. We have studied the changes of the mechanical properties of rubbers during heating at different temperatures in this kinetic range.

It is evident from Figure 4 that, at all the temperatures studied, the moduli of the rubbers increased progressively. Consequently the thermal structure of butadiene rubbers which is built up at a double bond of the side chains develops without the aid of oxygen.

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VULCANIZATION OF RUBBER *

N. L. NEMIROVSKIĬ

Despite the great practical importance of the vulcanization process, the most fundamental process in the rubber industry, its nature is not yet satisfactorily explained.

At the present time the well known bridge theory of spatial chain formation appears to have received the widest acceptance. According to this theory, filiform rubber molecules are linked together chemically during vulcanization by means of the vulcanizing agent, with formation of a new kind of sulfur bridge or other bridge, whereby the rubber molecules are "sewed" together, so to speak, by these intermolecular chemical bonds. The prevailing theory explains the change of physical-mechanical properties of rubber during its reaction with a vulcanizing agent. In fact, the formation of such spatial structures can explain the change of the physical-mechanical properties of rubber. However, it is hard to make experimental data agree with the bridge theory of vulcanization.

EXPERIMENTAL PART

VULCANIZATION OF NATURAL RUBBER WITH IODINE

In these experiments rubber mixtures of the following compositions by weight were investigated.

Rubber (smoked sheet)	100	100	100	100	100	100
Iodine	0.1	0.5	1	3	5	7.5
Ethyl alcohol	10	10	—	—	—	—
Barium carbonate	25	25	25	25	25	25

For the most uniform dispersion of iodine in the rubber, solid iodine was ground in a mortar with barium carbonate, and alcohol was added to various small amounts (0.1–0.5 per cent) of iodine, and the ingredients were then mixed on a cold roll mill. Each mixture was put into a mold with a slight excess of volume, which assured complete filling of the mold with the mixture and most effectively removed atmospheric oxygen from the mold. When heated with a large quantity of iodine, the rubber decomposed and became a resinous mass. With 0.1–1 per cent of iodine, vulcanization was not appreciable. The results of experiments on vulcanizates containing 3–7.5 per cent of iodine are given in Tables 1, 2, and 3.

In all the experiments there is a noticeable increase of the relative and permanent elongation. The resistance of the vulcanizates to swelling in benzene is noteworthy. At 160° C the swelling decreases 148 per cent, and becomes roughly equal to that of sulfur vulcanizates.

Examination of the solvent after swelling of the vulcanizates showed that none of the vulcanizate had dissolved.

The data obtained for the changes of the properties of rubber due to the action of iodine clearly indicate that iodine is a vulcanizing agent for rubber.

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Journal of Applied Chemistry (Zhurnal Prikladnoi Khimii)*, Vol. 24, No. 6, pages 674–677, June 1951.

TABLE 1

EFFECT OF DIFFERENT IODINE CONTENTS ON THE VULCANIZATION OF RUBBER
(Heating time 10 minutes; temperature 120° C)

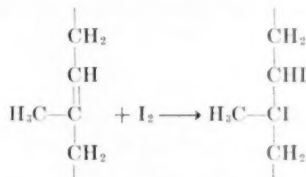
Iodine content (%)	3	5	7.5
Tensile strength (kg. per sq. cm.)	9.7	12	13.7
Relative elongation (%)	1130	910	403
Permanent elongation (%)	63	51	12
Swelling in benzene for 24 hours (%)	1068	920	740

TABLE 2

EFFECT OF CHANGE OF TEMPERATURE ON THE VULCANIZATION OF RUBBER
(Iodine content 7.5 per cent; vulcanization time 100 minutes; temperature (° C))

Temperature (° C)	100	120	140	160
Tensile strength (kg. per sq. cm.)	12	13.7	15.2	36.5
Relative elongation (%)	543	403	307	55
Permanent elongation (%)	18	12	5	0
Swelling in benzene for 24 hours (%)	1026	740	530	148

As is well known, the reaction involved in the absorption of iodine into unsaturated hydrocarbons proceeds according to the following scheme:



In view of these results and the mechanism of the action of iodine, we must conclude that the effect of vulcanization (formation of soft rubber) depends on the intramolecular saturation of the double bonds of the hydrocarbon by the vulcanizing agent.

TABLE 3

EFFECT OF TIME ON HEATING ON THE VULCANIZATION OF RUBBER
(Iodine content 75%; temperature 140° C)

Experiment	Time (in minutes)		
	15.2	16.1	33
Tensile strength (kg. per sq. cm.)	307	120	62
Relative elongation (%)	5	1	0
Permanent elongation (%)			

VULCANIZATION OF RUBBER WITH HIGH PROPORTIONS OF SULFUR

Vulcanization of rubber with large proportions of sulfur enables us to study the changes of the mechanical properties of rubber at every stage of the vulcanization from soft rubber to hard, horny ebonite.

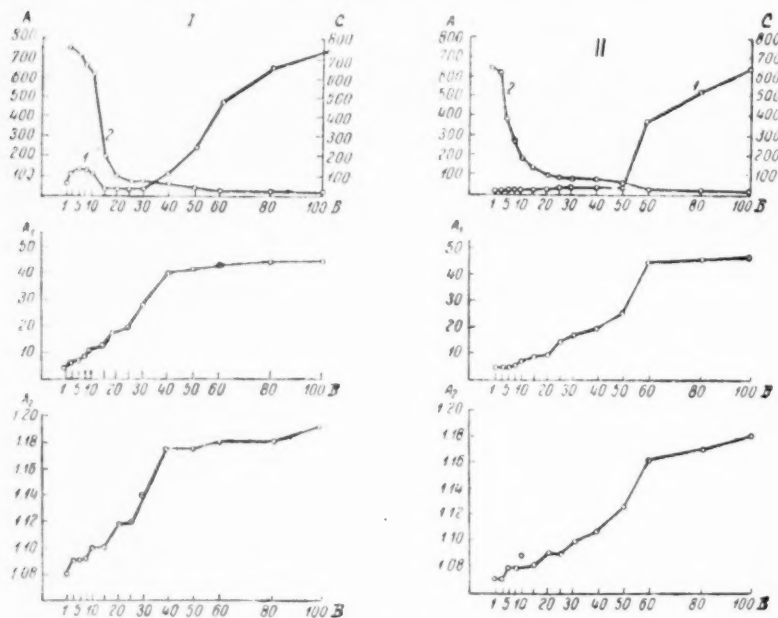
The rubber mixtures had the following compositions (by weight):

Rubber (smoked sheet)	100	—
Sodium-butadiene rubber	—	100
Sulfur	50	50
Diphenylguanidine	2	2

Vulcanization was carried out in a steam press at 147° C for periods of 1, 3, 5, 7, 10, 15, 20, 25, 30, 40, 50, 60, and 80 minutes.

The results of the mechanical experiments and analyses are shown in the figure.

The mechanical properties of the natural rubber vulcanizates are almost the same as those of the sodium-butadiene rubber vulcanizates, if the 1-15 minute period of vulcanization, during which significant differences of mechanical



Mechanical properties of vulcanized rubber as a function of the proportion of bound sulfur and of the specific gravity of the rubber mixture

I Diagrams of natural rubber

II Diagrams of sodium-butadiene rubber

A Tensile strength (kg. per sq. cm.)

A₁ Sulfur content (per cent)

A₂ Specific gravity

B Time (minutes)

C Elongation at rupture (per cent)

Curves marked 1 represent tensile strength; curves marked 2 represent per cent elongation at rupture

properties appear, is disregarded. At higher degrees of vulcanization the vulcanizates are hardly distinguishable from each other.

Within a period of 15 to 30 minutes for natural rubber and 1 to 50 minutes for sodium-butadiene rubber (SKB), the tensile strength (about 20 kg. per sq. cm.) hardly changes, despite the considerable increase of bound sulfur (up to 26-28 per cent on the rubber). This lends support to the assumption that the intermolecular chemical reactions of rubber and sulfur, *i.e.*, the formation of bridges, are practically absent at this particular stage of vulcanization (formation of soft rubber). Rebinder and Pisarenko¹ agree with this. They believe that, according to the bridge theory, it would be necessary to expect an increase

of tensile strength of vulcanized SKB with increase in the proportion of sulfur; however, no increases of tensile strength were discovered even when large percentages of sulfur were added to the SKB. At the same time, Rebinder and Pisarenko¹, observing that 90-98 per cent of the bound sulfur does not take part in the formation of bridges, point out the great importance of the sulfur which reacts with the rubber intramolecularly, forming polar groups, whose evolution they consider a fundamental cause of the change of the physical-mechanical properties of rubber during vulcanization.

Without minimizing the importance of the polar groups, we cannot consider their formation a fundamental cause of the change of the properties of rubber during vulcanization.

The formation of polar groups, as well as of bridges, does not explain the above-mentioned progressively decreasing tensile strength of vulcanizates, despite the greatly increased quantity of bound sulfur, and, consequently, of polar groups.

In the opinion of this author, the following factors must be studied here:

(1) the character of the union of the molecules in the rubber, which presents an interwoven system of relatively long filiform molecules situated at very short distances from one another;

(2) the change of the form of the filiform rubber molecules as a result of their reaction with sulfur and, consequently, the shrinkage which the whole system undergoes. This shrinkage is confirmed by the experimental data (see the accompanying figure);

(3) the formation in the rubber molecules of deformed and stretched states.

In his work on rubber, Buizov² attached great importance to its shrinkage during vulcanization, and considered the increased specific gravity resulting from shrinkage of the whole mass the true explanation of the nature of the vulcanization process.

During a vulcanization period of 30-100 minutes for natural rubber and 50-100 minutes for sodium-butadiene rubber, there is a large and sharp increase of tensile strength. At this stage of vulcanization the rubber is transformed from a soft elastic state to a hard horny product (ebonite), which possesses extremely high mechanical properties. The formation of such a product, in distinction from soft rubber, is easily explained by the intermolecular chemical reactions of knitting together of the filiform rubber molecules into a stable system. This view is confirmed by the large increase of tensile strength of rubber, during the formation of ebonite, for only a slight increase of bound sulfur.

CONCLUSION

The phenomenon of the vulcanization of soft rubber can be regarded as an intramolecular reaction.

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RELATION BETWEEN STRESS RELAXATION AND AGING RESISTANCE OF RUBBER VULCANIZATES

SOME PRELIMINARY INVESTIGATIONS *

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INTRODUCTION

The intimate relation between the oxidation of a vulcanized rubber matrix and the rate of stress relaxation at constant strain is now a well established fact, as pointed out by Tobolsky¹ and others.

As stress relaxation determinations can be completed in a few hours, it was very tempting to use such measurements at relevant temperatures rather than the tedious long-lasting routine aging tests.

To obtain information we investigated four typical compounds selected to cover the known range of aging stability of accelerated stocks with inert fillers. The results tabulated are given empirically, as it is considered that present knowledge of the structure of the vulcanized rubber matrix containing accelerators is inadequate.

THE MODULUS BALANCE

By courtesy of A. V. Tobolsky we obtained a set of drawings of the original Firestone balance and built a model ourselves. This balance was unsatisfactory, as the ratio 1:10 of the arms was slightly inaccurate and required a complicated set of corrections. We therefore built a balance with equal arms, using the beam and bearings of an ordinary 250-gram analytical balance, as shown in Figure 1A. The beam could be loaded to 1500 grams.

The first series of tests did not agree well, due to an uneven strain in the two parts of the test ring. The shaft for the lower roller was afterward mounted in a SKF ball bearing (a).

This arrangement affected an automatic equal distribution of the strains. The indication of the zero point of the balance was performed by means of a platinum contact with a stout platinum wire soldered in a hole bored in a small brass cylinder in such a way that only 0.3 mm. of wire projected from the support cylinder (b). The signal current was amplified in the relay (c), which actuated a red lamp and a bell. The weights were in the form of discs and were stacked one upon another to facilitate changing (500, 250, and 50 grams units).

The balance was housed in the thermostat as shown. The fan (c) forced the air from the balance compartment over the heating lamp. The temperature variation was $\pm 0.2^\circ \text{C}$.

COMPOUNDS AND TEST SPECIMENS

Originally the test rings (Schopper type, 52.6 mm. outer diam., 44.6 mm. inner diam.) were cut from 1-mm. slabs, using either the ICI-cutter² (revolving

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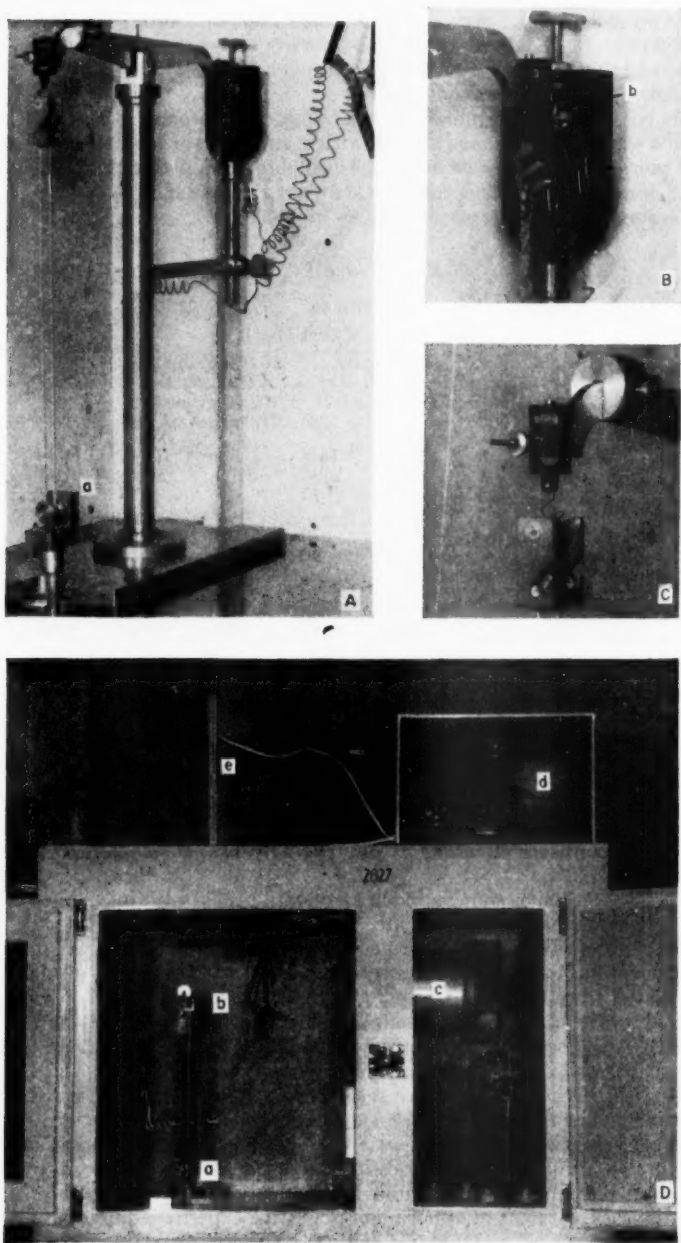


FIG. 1.—The modulus balance. (A) Detail of balance. (B) Detail showing contact. (C) Detail showing upper roll. (D) Thermostat and alarm relay.

with two razor blades, cutting the test ring in one operation) or the Schopper 3-die cutter. R. D. Andrews suggested the use of a cutter with two concentric blades, and this type of cutter was used throughout the work. The inner blade was about 0.2 mm. higher than the outer.

The compounds were mixed on a laboratory mill for a 2-kilogram charge. All slabs were cross-plied and dusted with a minimum of talc (this is essential) before vulcanization between hard, polished aluminum plates at $152^\circ \pm 0.5^\circ \text{C}$, using 1 mm. spacers. The resulting slab was then circular.

The formulas of the stocks are given in Table I.

TABLE I

STOCKS

Common Master Batch

Smoked sheet 1 extra.....	10,000 grams
Zinc oxide (Red Seal).....	1,000 grams
Whiting (Kragelund).....	10,000 grams
Total.....	21,000 grams

Stock no.	I-	I+	II-	II+	III-	III+	IV-	IV+
Batch	2100	2100	2100	2100	2100	2100	2100	2100
Sulfur	15	15	15	15	15	15	—	—
DPG	20	20	—	—	5	5	—	—
Stearic acid	—	—	10	10	10	10	10	10
MBTS	—	—	20	20	20	20	—	—
TMT	—	—	—	—	—	—	30	30
PBN	—	20	—	20	—	20	—	20
Whiting	85	65	75	55	70	50	80	60
Total	2220	2220	2220	2220	2220	2220	2220	2220

All compounds 45% smoked sheet by weight.
 DPG, diphenylguanidine (Monsanto). MBTS, benzothiazolyl disulfide (Thiofide, Monsanto). TMT, tetramethylthiuram disulfide (Sharples). PBN, phenyl- β -naphthylamine (Neozone-D, du Pont).
 The Danish whiting contains about 0.06% manganese and 0.003% copper in inactive form.
 The stocks were all cured to maximum tensile strengths.

The aging tests were run at 70°C in circulating air, using a German slab type VDM No. 2, with 5 mm. width at the narrow part. The slabs were about 2 mm. thick; 3 specimens were used and the results averaged. From the tensile-time graph the time required for the TB to fall to one-half its value was computed ($t_{1/2}$ TB).

The test-specimens were stored in cardboard boxes in the oven, piled so as to keep the narrow part free in the air.

The stress relaxation measurements were carried out at 110°C at 200 per cent elongation. The modulus at 6 seconds after the start of straining was interpolated from the M^{200} vs. $\log t$ graph, as shown in Figure 2. This value was used for the calculation of the $t_{1/2}$ time for the M^{200} , which value in minutes at 110°C was used as a measure of the stability of the vulcanizate to aging. The aging and stress relaxation data are compared in Table II.

From the data cited it will be seen that the agreement between the stress relaxation and aging data is fairly good, the coefficients of retardation especially showing a very satisfactory value. Stocks II and III have different stabilities according to whether these are estimated by stress relaxation or by aging. Such anomalies often occur in rubber investigations and can be checked only by statistical treatment of a more representative experimental material.

The temperature variation of $t_{1/2}(M^{200})$ was determined as in Table III for compound I.

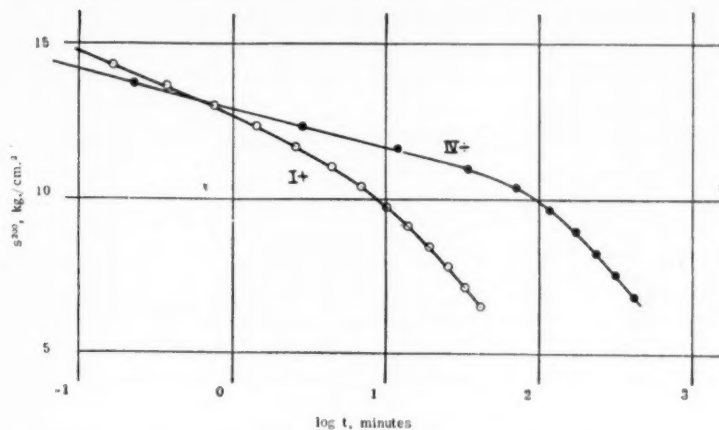


FIG. 2.—Extrapolation of the modulus at 200 per cent to 6 seconds.

TABLE II
STRESS RELAXATION AND AGING DATA

Stock	S	Accelerator	Anti- oxi- dant	Cure at 152° C (min.)	TB ^b kg./ sq.cm.	EB ^b (%)	$t_{1/2}(M^{200})$ min./ 110° C	$t_{1/2}(TB)$ days/ 70° C	ϕ^c	ϕ^d
I—	1.5	DPG 2 ^a	—	7	147	565	9.3	10	1070	
I+	1.5	DPG 2 ^a	2	7	158	550	29.5	40	310	3.4
II—	1.5	MBTS 2	—	14	171	580	22	31		
II+	1.5	MBTS 2	2	14	184	600	48	117	3.8	
III—	1.5	MBTS 2								
		DPG 0.5	—	5	175	540	56	27		
III+	1.5	DPG 0.5	2	5	198	565	112	67	2.5	
IV—	0	TMT 3	—	15	161	540	380	80		
IV+	0	TMT 3	2	15	180	580	1200	300-600	3.8	

^a Figures: per cent based on the rubber.^b Zero values from the aging tests.^c Coefficients of retardation (antioxidant function).^d Cf. reference 1.^e Initial rates of oxidation, measured manometrically, moles oxygen per gram smoked sheet per hour ($\times 10^{-7}$).

The plot in Figure 4 shows a perfectly linear Arrhenius line, giving a value for the energy of activation of 24,000 calories, while a value determined previously for the rates of oxidation was about 20,000 calories.

Addition of 0.012 per cent copper as stearate decreased the $t_{1/2}(M^{200})$ values for I— to 8.0 minutes (I—/—9.3) (—/—: antioxidant-copper) and for I+

TABLE III
 $t_{1/2}(M^{200})$, MIN.

° C	(T)	1000/T	t	2 - log t
90	363	2.754	54.3	0.265
100	393	2.684	22.6	0.649
110	383	2.610	9.8	11.008

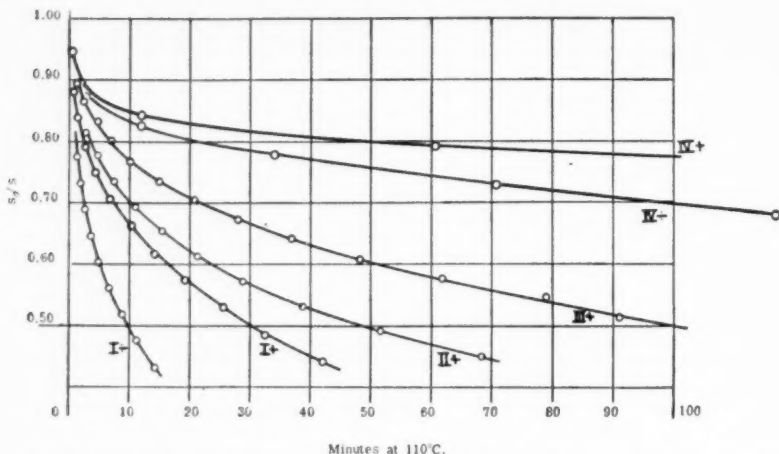


Fig. 3.—Relative stresses at 110°C. (I) DPG compound. (II) Thiofide compound. (III) Thiofide boosted with DPG. (IV) Sulfurless thiuram compound (—) Denotes absence of antioxidant. (+) Denotes presence of 2 parts Neozone-D (per cent based on the rubber).

to 22 minutes ($I+/-29.5$), which is a rather low copper effect compared with the influence on the initial rate of oxidation. This might be increased for $I-$ from about 1000 to 5700 with 0.01 per cent copper. In any case the measurement of oxidation is the more sensitive method for the evaluation of copper effects in vulcanized rubber³. In Figure 4 the rates of oxidation are plotted for comparison.

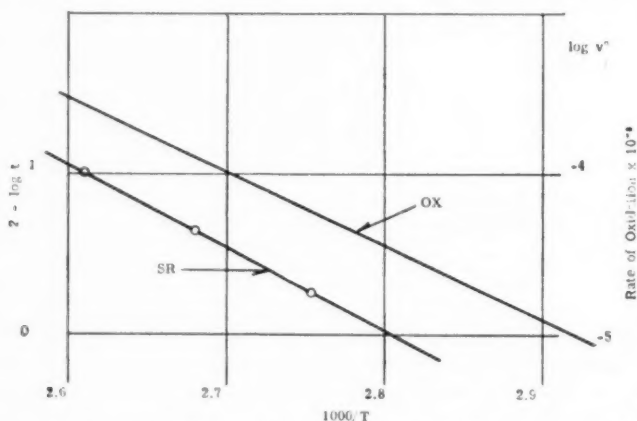


Fig. 4.—Temperature coefficient. (SR) Rate of relaxation. (OX) Initial rate of oxidation in moles oxygen per gram rubber per hour (measured manometrically).

ACKNOWLEDGMENT

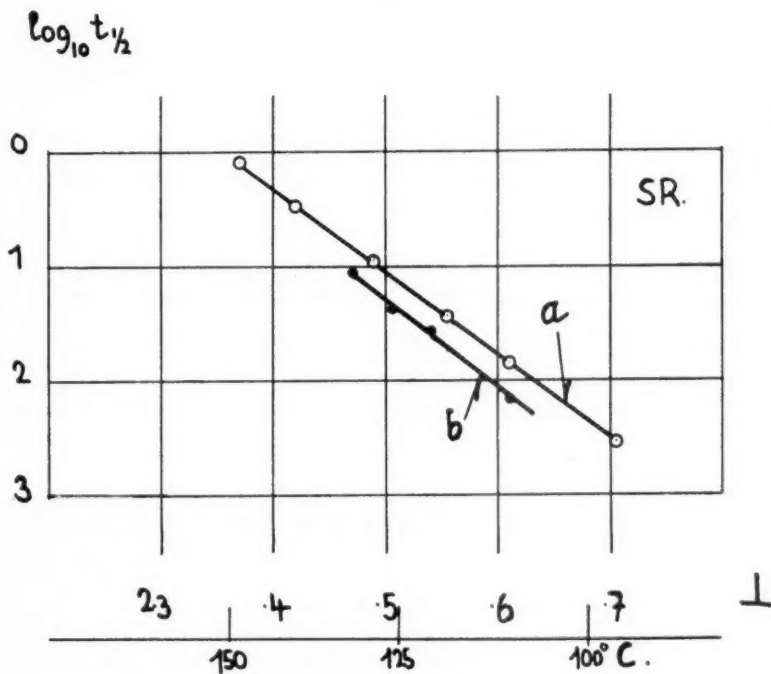
Finally we wish to express our thanks to our firm for permission to publish this paper, and further thanks to N. Hofman-Bang, R. D. Andrews, and R. Mesrobian for helpful suggestions during the course of the work, and to A. F. R. Smith, I.C.I. (Export), Ltd., who was kind enough to correct the language.

SUMMARY

In this paper some details are given for the construction of a simple balance for the measurement of stress relaxation at constant elongation. A simple means of obtaining equal strain in two parts of the strained specimen is provided. By means of four typical stocks, covering the widest possible range of aging resistance, it is shown that the stress relaxations give approximately the same estimate of stability as does the normal Geer test using 2-mm. dumbbell specimens. As a measure for stress relaxation, the time is used that is required to obtain 50 per cent of the value of the interpolated modulus at 200 per cent elongation 6 seconds after the straining zero time at 110° C. The parameter for the aging test is the time in days at 70° C for the 50 per cent value of tensile strengths. The range for the stress relaxation parameter may be estimated to 8–1200 minutes and the aging parameter from 10–600 days. Finally the concordance of temperature coefficient for relaxation and oxidation rates is shown.

APPENDIX

Since the time that the preliminary experiments were carried out, the following changes of some details of the technique have been introduced. The upper roller is placed freely revolving on two pin screws as an interchangeable element fitted with locking nuts on the screws. The balance is placed on the top outside



APPENDIX. FIG. 1.—Temperature functions for relaxation at about 170 per cent elongation. Standard whitening batch. 0.9 mm. rings. a. 0.5 sulfur, 2 diphenylguanidine, 1.5 Neozone-D. Cure 4 min. at 162° C. b. 2 MBTS, 2 sulfur, 1.5 Neozone-D. Cure 6 min. at 162° C.

the thermostat. This arrangement facilitates operation of the weight appreciably. The lower contact platinum plate is replaced by a microglass with mercury covered with a drop of glycerol to avoid oxidation by sparking.

Further to increase the reproducibility of the results, all test rings are marked in the same position relative to the cutter and suspended in exactly the same position. The elongation is reduced to approximately 170 per cent, corresponding to 200 mm. center distance with 0.9 mm. rings and 7 mm. diameter of the roller.

The temperature variation of $t_{1/2}(M\ 170\%)$ is shown in the figure of this Appendix for two different compounds, of which compound *a* was measured over a rather large temperature range. The linearity of the Arrhenius line is almost perfect. The relaxation times here encountered are so small that the rate of oxidation can be assumed to be constant, as earlier confirmed by manometric measurements.

In Table I of this Appendix some measurements are tabulated to show a sort of spectrum of stability as a relation between $t_{1/2}(M\ 170\%)$ in minutes at

TABLE I

	No.	Sulfur (% based on the rubber)	Accelerator (% based on the rubber)		Anti- oxi- dant (Neo- zone-D) (% based on the rubber)	Vulcanization		$t_{1/2}(M)$ min. 121°	$t_{1/2}(TB)$ days 70°
						(min.)	(° C)		
50	100	3	MBT	2	1.5	3	162	37	27
50	101	2	MBT	2	1.5	11	162	105	76
50	102	1	MBT	2	1.5	7	162	98	550
50	103	3	MBTS	2	1.5	5	162	22	39
50	104	2	MBTS	2	1.5	6	162	36	54
50	105	1	MBTS	2	1.5	8	162	80*	(160*)
50	106	1	MBT	1	1.5	7	162	102	135
			MBTS	1					
50	43	0.1	TMT	3	2	12	152	627	210
50	47	0.1	TMT	22	2	13	152	488*	350
50	61	0	TMT	3	2	17	152	1148*	(260*)
			Te	1					
50	63	0	TMT	2	2				
			Te	1	2	8	163	977*	770*
51	61	1	Sc	1	1.5	7	162	79	97
51	86	0.5	DPG	2	1.5	4	162	20	10.5

M, modulus at 170% elongation. Asterisk, interpolated value. Brackets denote uncertain value. MBT, Thiotax (Monsanto), mercaptobenzothiazole. MBTS, Thiofide (Monsanto), mercaptobenzothiazole disulfide. TMT, Thiuram (Sharples), tetramethylthiuram disulfide. Te, tellurium, Telloy (Vanderbilt), Neozone D (du Pont), phenyl- β -naphthylamine. Sc, Santocure (Monsanto), cyclohexyl salt of MBT, DPG, diphenylguanidine (Monsanto). The vulcanization times correspond approximately to optimum tensile strength values for 2 mm. slabs.

All the compounds are mixed from a common masterbatch containing:

smoked sheet	1000
stearic acid	10
zinc oxide	100
whiting (Kragelund)	1065
	2175

thus giving approximately 45 per cent rubber by weight.

121° C and the $t_{1/2}$ (TB) in days at 70° C, the latter obtained by oven aging in circulating air, using dumbbell specimens. It is seen that the numerical values and the order of ranging are about the same. The effect of increasing proportions of sulfur with constant concentration of accelerator is well demonstrated with MBT and MBTS. We have made further experiments with Zimates and a number of binary and ternary combinations of thiazoles with boosters and various fillers, which have raised some difficulties of interpretation. We might, therefore, finally state that the method is doing the best service with compounds which do not differ too much in the structure of vulcanization.

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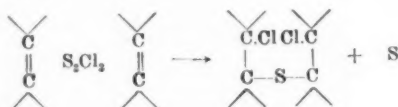
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DILATOMETRIC MEASUREMENT OF THE RATE OF VULCANIZATION OF CREPE RUBBER BY SULFUR MONOCHLORIDE *

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The cold vulcanization of rubber by sulfur monochloride is believed to consist essentially of the cross-linking of adjacent polyisoprene units by a series of sulfide bonds. Chemical analysis of the product¹ suggests that the cross-linking process is analogous to the mustard gas reaction of ethylene with sulfur monochloride, thus:



Nothing is known, however, about the kinetics of this vulcanization process. General considerations lead one to expect that such a reaction, involving polymer aggregation, should be accompanied by an increase in the density of the rubber; moreover, by choosing a suitably delicate technique, it should be possible to utilize such density changes for rate determinations. A dilatometric method seemed most suitable, and the experiments described here show that the vulcanization process is, indeed, accompanied by a decrease in volume of the reaction mixture, and that the reaction may be followed quantitatively using a tap dilatometer².

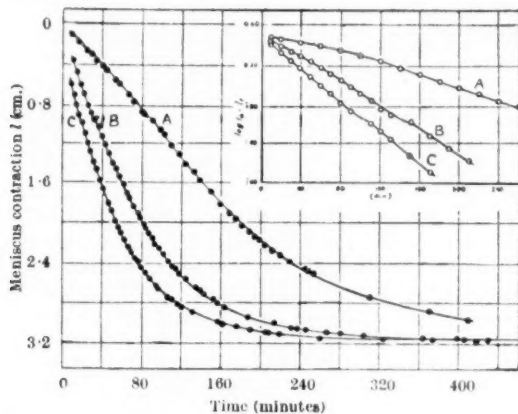
When a 0.2 per cent dispersion of crepe-rubber in benzene was treated with an excess (1.4 per cent) of sulfur monochloride, a slow contraction was observed in the dilatometer. This slow contraction was accompanied by the development of a slight Tyndall effect. After completion of the contraction, the Tyndall effect slowly developed into a precipitate of vulcanized rubber, the precipitation process being characterized by a slight increase in the volume of the system. The accompanying graph shows three typical kinetic runs (25°) using purified crepe-rubber dispersed in thiophene-free benzene, twice-distilled sulfur monochloride, and different amounts of an organic accelerator consisting of dibutylammonium thiocarbamate, 34 per cent, 2-mercaptobenzthiazole, 21 per cent, Cellosolve, 45 per cent. Details are given in the accompanying table.

Expt.	[S ₂ Cl ₂] %	[Accelerator] %	k ₁ min. ⁻¹
A	1.38	zero	0.0078
B	1.41	0.0204	0.0152
C	1.38	0.0352	0.0189

From the graph, it is clear that the unaccelerated reaction (A) is characterized by a slow initial reaction which develops, after about 120 minutes, into

* Reprinted from *Nature*, Vol. 167, No. 4245, pages 404-405, March 10, 1951.

a first-order reaction. In the presence of small amounts of the accelerator, two effects are evident: the slow initial reaction is virtually eliminated as a rate-determining factor, and the rate coefficient (k_1) of the subsequent first-order reaction is markedly increased. The inset figure is a logarithmic plot and it shows both the catalytic effect of the accelerator, and the extended region of the first-order portion of the reaction from 55 per cent of total reaction in A to 80 per cent in C. The latter value covers the whole of the region observed experimentally.



Reaction-time curves for the vulcanization of crepe-rubber (0.2 per cent) in benzene by sulfur monochloride. A, unaccelerated reaction. B, C, accelerated reactions. Temperature, 25.0° C. Inset. Logarithmic plot showing extension of first-order region in the presence of accelerator (B, C).

These results present the possibility of a kinetic investigation into the mechanism of the cold vulcanization process, together with a study of the function of organic accelerators. Such an investigation has now been initiated and the results will be published in due course. Theoretical aspects are held over pending further study.

Thanks are due to J. H. Schulman for helpful discussions and to the Chief Scientist, Ministry of Supply, for permission to publish this communication.

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EFFECT OF TEMPERATURE AND RATE OF STRETCHING ON THE TENSILE STRENGTH OF VULCANIZATES *

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According to our theories, the molecular chains in vulcanized rubber are bound by: (1) forces of primary valences, and (2) intermolecular forces of a different nature and intensity, located in different parts of the hydrocarbon chain, and also in the oxygen- and sulfur-bearing groups contained in the chain¹. Here also should be included the hydrogen bonds which can form as a result of the presence of carboxyl and hydroxyl groups in the vulcanizate².

The tensile strength of a vulcanizate depends on the number and character of the bonds, which are deformed by the rupture, as well as on the structure of the vulcanizate, density and uniformity of the spatial network³, tendency to crystallize, and orientation on stretching⁴. In the absence of a uniform spatial network, plastic deformation may take place, which essentially changes the type of rupture and, consequently, the tensile strength of the vulcanizate.

All the factors mentioned depend in varying degrees on the temperature and other experimental conditions. Thus, for example, an increase of the temperature to 60–80° C greatly weakens the intermolecular and hydrogen bonds, slightly affecting the chemical bonds. On this basis, observations of the decrease of tensile strength with rise in temperature made by the authors⁵ and other investigators⁶ were used to explain in some measure the nature of the bonds in rubber and its vulcanizates. Some of the results of our efforts are the subject of this article.

Butadiene-styrene rubber was the subject of investigation, because it does not crystallize during stretching nor give a relatively strong rubber without the use of an active filler.

The rubber mixtures were prepared according to two recipes, the second of which gave vulcanizates in which thermally stable monosulfide intermolecular bonds were more likely to be present.

	Mixture 1	Mixture 2
Rubber	100	100
Sulfur	2	—
Zinc oxide	5	5
Tetramethylthiuram disulfide	0.5	3

Each mixture was dissolved in benzene and from the solution obtained, sheets of thickness 0.10–0.16 mm. were prepared on glass ampules by dipping. Vulcanization was carried out in carbon dioxide gas for 30 minutes at 142° C for mixture No. 1, and 40 minutes for mixture No. 2; these periods represent the optimum times of vulcanization for the mixtures. After vulcanization, ten rings of 5.2 mm. were cut from the sheets with a specially designed knife

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Colloid Journal* (*Kolloidnyi Zhurnal*), Vol. 13, No. 4, pages 267–272; July–August 1951.

and were subjected to rupture in the experiment. The use of rings enabled us to keep the specimens from slipping out of the dynamometer clamps.

The tensile strength experiments were performed at three rates of deformation: 1.3, 10.3, 100, and 1000 mm. per minute, which represent 2.5, 19.7, 191.5, and 1915 per cent per minute. Stretching at the lower two rates (1.3 and 10.3 mm. per minute) was carried out in a precision dynamometer⁷ and at the two higher rates (100 and 10000 mm. per minute) in a Smirnov dynamometer. The experimental conditions in the latter case were approximated to those in the precision dynamometer (slow movement of the upper clamp and rate of stretching equal to the rate of movement of the lower clamp).

The results obtained, given in Figures 1 and 2, show that the two mixtures behave almost alike. The tensile strength, calculated on the actual cross-

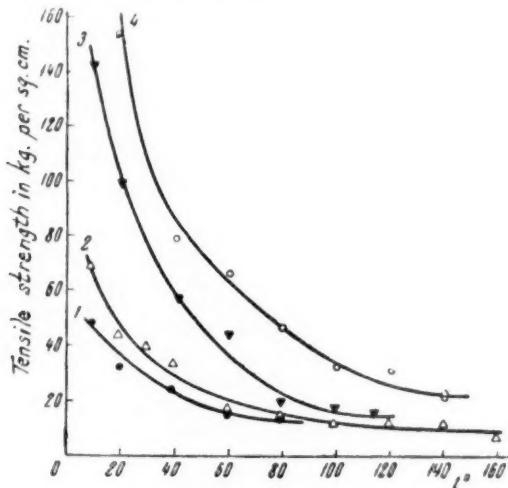


Fig. 1.—Change of tensile strength (based on the actual cross-section) with temperature for different rates of elongation. (Mixture No. 1.)

Curve 1. 1.3 mm. per minute.
Curve 2. 10.3 mm. per minute.
Curve 3. 100 mm. per minute.
Curve 4. 1000 mm. per minute.

section, and the ultimate elongation decrease with rise of temperature at all rates of elongation studied, although these decreases were observed only up to 80–100° C for three of the rates of stretching—from one to 1000 mm. per minute. When the temperature is raised still higher, the tensile strength hardly changes, whatever the rate of stretching. At the highest rate studied (1000 mm. per minute), the decrease of tensile strength ceases with a slight rise of temperature.

With an increase of the rate of stretching, tensile strength and elongation at rupture at temperatures up to 100° C also increase. This relationship for the tensile strength can be expressed by the equation: $\Pi = av^n$, where Π is the tensile strength of the actual cross-section, v is the rate of elongation, and a and n are constants. The applicability of this equation (in logarithmic form) is confirmed by Figure 3. At temperatures above 100° C and rates less than 100 mm. per second, the tensile strength and ultimate elongation are practically independent of the rate of elongation.

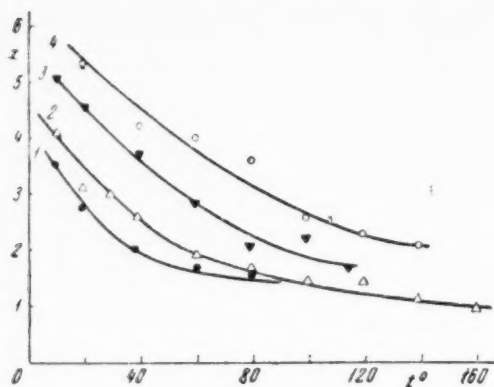


FIG. 2.—Change of elongation at rupture with change of temperature at different rates of stretching. (Mixture No. 1.)

Curve 1. 1.3 mm. per minute.
 Curve 2. 10.3 mm. per minute.
 Curve 3. 100 mm. per minute.
 Curve 4. 1000 mm. per minute.

The results obtained, it seems to us, can be interpreted thus. The tensile strength, which is not dependent on the mechanism of the phenomenon, undoubtedly depends on segments of the molecular chains which are partially oriented up to the moment of rupture. In the case of natural rubber, the partially oriented segments constitute the crystalline phase and, as Lukin and Kastrochkin⁸ showed in our laboratory, with *x*-ray data, the tensile strength increases approximately linearly with the number of crystals. The *x*-ray data also indicate that a decrease of the rate of elongation, and, likewise an increase of the temperature lead to a decrease of the crystalline phase. This decrease can be explained by the relaxation processes of deorientation of the chains which take place during elongation and which increase as the temperature increases and as the rate of stretching decreases. Such an explanation of the change of tensile strength with temperature and rate of stretching is confirmed by the change of the ultimate elongation, which increases as the temperature

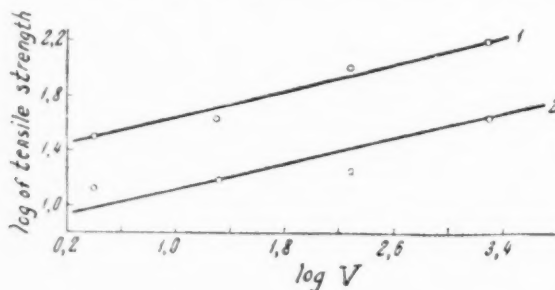


FIG. 3.—Tensile strength (based on the actual cross-section) as a function of the rate of stretching. (Mixture No. 1.)

Curve 1. 20° C.
 Curve 2. 80° C.

decreases and as the rate of elongation increases in the temperature interval up to 100° C. If plastic flow had taken place as a result of the displacement of the mass of chemical chains, then a reverse dependency would have been observed.

As was shown in work of Dogadkin, Bartenev, and Reznikovskiy², relaxation processes in rubber within a certain temperature range are connected with the destruction and regrouping of the local intermolecular bonds among the rubber chains. Naturally, these bonds are greatly weakened when the temperature is raised. Consequently, the conditions of formation and decomposition of the partially oriented segments of the molecular chains in rubber also change. The decrease of intermolecular energy is especially great in the temperature range up to 80–100° C. This same range is also characterized by sharper decreases

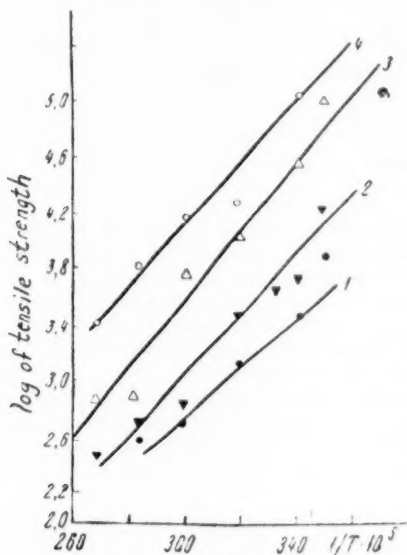


FIG. 4.—Logarithmic tensile strength relation. (Mixture No. 1.)

Curve 1. 1.3 mm. per minute.
Curve 2. 10.3 mm. per minute.
Curve 3. 100 mm. per minute.
Curve 4. 1000 mm. per minute.

of tensile strength of the vulcanizates. A further rise of temperature has very little effect on the tensile strength, inasmuch as the chemical bonds in the vulcanizate are not broken at these temperatures. Also, where the change to the region of independence of tensile strength and temperature is observed, the rate of elongation increases with rise of temperature. This phenomenon becomes understandable if we remember that the rate of elongation and the temperature influence the relaxation processes of deorientation of the chains during stretching.

In order to explain the nature of the bonds which are destroyed by the action of the temperature, it is useful to ascertain whether the decrease of tensile strength with temperature follows a regular pattern analogous to the equation of Arrhenius.

From Figure 4 it is evident that at all rates of elongation a relationship is observed which can be expressed formally by the equation:

$$\Pi = \Pi_0 e^{U/RT}$$

where Π is the tensile strength in kg. per sq. cm. of the actual section, R is the gas constant, T is the absolute temperature, and Π_0 and U are constants.

The constant U , which is in terms of energy, is a measure of the decrease of tensile strength with temperature. The faster is this decrease, the greater is U , and, evidently, the greater the weakening of the intermolecular bonds during heating and the greater their influence on the tensile strength.

TABLE I
VALUE OF THE CONSTANT U FOR DIFFERENT RATES OF STRETCHING

Rate of stretching (mm. per min.)	Vulcanizate No. 1 (kcal. per mole)	Vulcanizate No. 2 (kcal. per mole)
1.3	3.8	3.5
10.3	4.6	4.3
100.0	4.2	4.9
1000.0	4.3	4.2

In Table I are given the values of the constant U for both mixtures, calculated for different rates of stretching with respect to the decrease of tensile strength in the temperature interval 20–80° C. The nature of the bonds in both rubbers is obviously the same. For rates from 10.3 to 1000 mm. per minute, the constant U is practically independent of the rate. At smaller rates of stretching, the molecules can be deoriented even at low temperatures; for this reason the weakening of the intermolecular bonds during heating has less effect on the strength of the system.

In a similar manner, the values of U were calculated from the experimental data of Feldstein⁸ for oxidized sodium-butadiene rubber and from the data of Epstein for vulcanizates of sodium-butadiene rubber, natural rubber, polychloroprene, and Butyl rubber. These data are given in Table II

TABLE II
VALUE OF THE CONSTANT U FOR VULCANIZATES OF DIFFERENT RUBBERS

Rubber	Kcal. per mole	Rate of stretching (mm. per min.)
Butadiene-styrene	4.2	100
Sodium-butadiene	6.7	500
Natural rubber	1.8	500
Butyl	7.2	500
Polychloroprene	13	10
Oxidized sodium-butadiene	7.1	1

The values of U obtained accord with the corresponding values of intermolecular energy. The authors do not think, however, that such a calculation will provide the true value of the activating energy of rupture of the molecular bonds in the vulcanizate. As was noted previously, the rupture of rubber is not a simple disunion of structural elements in the direction of stretching, but is accompanied by structural changes, and the rupture of the various bonds is distributed through a rather long period of time. The mechanism of brittle rupture proposed by Griffiths, and by Aleksandrov, Zhurkov, and Bartenev¹⁰ is measured by the dynamics of spreading of the cracks, and the measured tensile

strength depends on these dynamics. The theory developed by the authors concerning the role of relaxation processes in structure formation up to the moment of rupture does not conflict with the conception of the mechanism of brittle rupture.

We are inclined to think that the spreading of the cracks in the vulcanizate proceeds chiefly in the amorphous and less in the oriented phase. The highly oriented part serves as an incentive to the development of cracks perpendicular to the direction of stretching, or, in other words, perpendicular to the direction of orientation of the crystals. For this reason, as the development of cracks in the highly oriented part increases, the tensile strength of the material also increases.

CONCLUSIONS

1. The tensile strengths of vulcanizates of butadiene-styrene rubber decrease sharply with rise of temperature in the interval from 10° to 80° C. Further rise of temperature up to 140° C only slightly changes this property.

2. The elongation at rupture changes in a like manner.

3. The tensile strength and also the elongation at rupture depend on the rate of stretching, i.e., they increase at temperatures up to 80° to 100° C with increase of the rate of stretching. The tensile strength relationship is expressed by a gradient function.

4. The relation of tensile strength to the temperature can be expressed in an approximate way by the equation:

$$\Pi = \Pi_0 e^{U/RT}$$

The values of U calculated for vulcanizates of various rubbers range from 1.8 to 13 kcal. per mole.

5. An explanation of the causes of the changes of tensile strength and elongation at rupture of vulcanized rubber when the temperature and rate of elongation are changed is offered.

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ELASTICITY OF SOFT POLYMERS

CONSTANT-STRESS ELONGATION TESTS *

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Although rubber is used principally in the vulcanized state, considerable quantities of gum rubber and other soft polymeric elastomers, plasticized or unplasticized, are used in the adhesive tape and rubber cement industries. Pressure-sensitive adhesives, solvent-activated cements, or binders for increasing the strength of paper tapes are in part, or in their entirety, comprised of such soft polymers. The utility of the adhesives, cements, or binders is dependent to a great extent upon their viscoelastic properties. In the course of usage they are subjected to stresses of widely different duration and magnitude, and the resistance to shock, or the ability to withstand static loads for a long time, is directly related to the elastic and viscous deformation under the stress conditions.

Until recently, few exact methods have been available for measurement of the viscoelastic properties of soft, unvulcanized polymers. True, plastometers are used to characterize gum rubbers, but highly plasticized rubbers are often so soft and tacky that they are difficult to mold into suitable plastometer test specimens. Then, too, plastometer data are difficult to interpret in terms of fundamental physical constants.

Soft polymers are most conveniently handled as films cast from solution or emulsion, and in this form can be cut into strips for testing by elongation methods. However, commercial stress-strain machines for rubber testing have not been satisfactory for testing these materials. This is due in part to lack of sensitivity, but a more serious objection is their limited time range of stress application. Soft polymers exhibit stress relaxation to a much higher degree than vulcanized rubber, and therefore their elastic behavior is highly time-dependent.

A study of the creep of the elastomers, *i.e.*, deformation at constant stress, offered the possibility of measuring the viscoelastic properties over a wide time range. By applying the same treatment to polymer creep curves which Taylor¹ used on the creep curves of glasses near the annealing temperature, it appeared that it might be feasible to segregate elastic deformation and viscous flow, and thereby characterize the materials in terms of elastic modulus and viscosity.

CONSTANT-STRESS APPARATUS

In the study of the creep of glass rods¹ and of fibers², the deformation is a very small fraction of the total length of the sample, and the decrease in cross-sectional area during the test is negligible. Elongation at constant load is substantially equivalent to elongation at constant stress. Creep curves have been obtained on rubber in shear³, but not until recently has constant-stress elongation been applied to highly stretchable materials⁴.

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To maintain constant tensile stress on a material having the high elongation of rubber, it is necessary that the load be reduced to conform with the decrease in cross-sectional area of the stretching film. Roth and coworkers⁴ have designed a testing machine which reduces the load mechanically to maintain a fixed stress on a rubber strip, and report a high precision of strain testing. However, fixed stress can be realized without resorting to complicated loading devices. If the rubber strip is stretched by means of a bob which is lowered into a liquid, buoyancy reduces the load as the film stretches. If the mean density



FIG. 1.—Tension weight. Truncated hyperboloid.

of the bob is adjusted to that of the liquid, and if the level of the liquid does not change, then constant stress is realized when the bob takes the form of a hyperboloid whose radius varies with height according to the relationship:

$$r = \frac{1}{L_o + H} \sqrt{\frac{W_o L_o}{\pi d}}$$

where r is the radius at height H , W_o is the total initial load, L_o is the length of the test specimen, and d is the density of the liquid and bob⁵.

Figure 1 shows a bob designed for an initial load of 50 grams, a density of 1.00 gram per cc., and a specimen length of 3.00 cm. It was machined from

Compreg, an impregnated, compressed wood laminate which has relatively low moisture absorption, an important consideration when water is used as the buoying liquid. The mean density of the bob was adjusted by drilling a hole in the base, adding weight, and sealing the cavity.

The bob was truncated at a height of 30 cm., limiting the maximum extension of the strip to 1000 per cent. The weight of the attachments between the bob and the test sample was adjusted to give a total initial load of 50 grams.

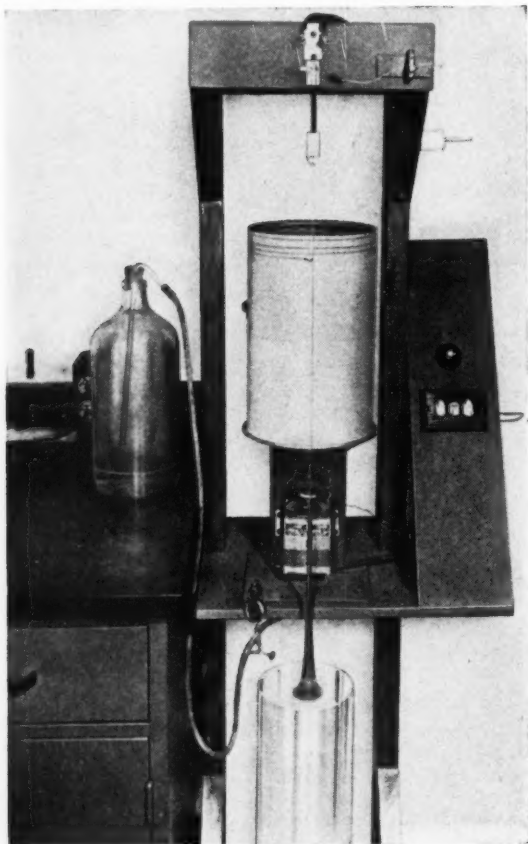


FIG. 2.—Constant-stress elongation tester.

The constant-stress elongation apparatus is shown in Figure 2.

The test strip is suspended vertically from the clamp holding the upper tab, and from the lower tab, which bears a metal eyelet, the bob is hung by a hook and wire. Before release, the bob is supported by a thread passing through the eyelet and over a resistance wire, and slack in the test-specimen is taken up by letting out the thread. The water cylinder, filled to overflowing, is raised by

means of a scissors-type auto jack (not shown) until the base of the bob is in the plane of the water surface.

The supporting thread is burned by the resistance wire, transferring the weight of the bob to the test strip, and the stretch is recorded by means of spark tracings on the kymograph. After a few seconds, the rate of elongation is usually reduced to such an extent that the spark tracings run together, and the stretch is then recorded manually by closing the spark circuit with a push-button switch at suitable time intervals.

PREPARATION OF TEST SAMPLES

All the measurements were conducted on films cast from organic solvent solutions or from water dispersions of the elastomers. In commercial applications the materials would be similarly deposited from solution or latex and would receive no subsequent mechanical treatment. Therefore cast films are representative of the condition of the materials in the finished products.

The test strips were cut from films deposited on tin panels which had been amalgamated with mercury to facilitate removal. To obtain films of sufficient thickness, in the neighborhood of 20 mils, the solutions (or latexes) were confined in retaining frames to permit drying of the required volumes. With volatile solvents such as heptane, benzene, or methylethyl ketone, it was necessary to slow the drying rate by means of covers; otherwise wrinkling occurred. The usual procedure was to dry the films for 24 hours under cover, then 24 hours uncovered. They were then lifted from the panels, dusted with talc, and dried 5 to 14 hours longer under vacuum at 50° C. The films were placed between sheets of waxed paper while the test strips were died out.

Any clamping devices which pinched the test strips were unsatisfactory because the soft films invariably failed at the clamps. The difficulty was overcome by cementing the ends of the strips into kraft paper tabs and applying the clamps to the tabs. Polyvinyl alcohol, applied as 10 per cent water solution, was found to serve very satisfactorily as a tabbing cement. There was no evidence of slippage in the tabs, and the exposed portion of the sample was taken to be the effective test length. The specimens were cut 4 cm. in length to allow for tab mounting.

REPRODUCIBILITY AND RANGE OF MODULUS VALUES

Sources of error are inherent principally in the measurement of the cross-sectional area of the test strip and in failure to note film defects. A high precision of strain measurement is achieved by the automatic recording device.

Errors in the cross-section measurement have been reduced by calculating the cross-sectional area from the length, weight, and density of the test-specimen, the density having been obtained from weight and volume measurements on a larger sample. Film defects are not often encountered, unless, because of rapid drying, waves or bubbles are formed. These defects lead to localized stress concentration which results in failure. Certain highly plasticized compounds, particularly those containing natural rubber, are troublesome in that they frequently neck down during stretching, although apparently free of defects in the unstretched state. GR-S and nitrile-rubber compounds are rarely subject to this type of failure.

The accuracy of the method is such that the effect of rather small changes in formulation can be detected. Differences exceeding 2 per cent have never

been encountered in the 10-minute moduli of duplicate samples cut side by side from the same film.

The apparatus described here, employing a 50-gram tension weight, is designed for materials whose 10-minute moduli fall in the range 0.2 to 3.5 megadynes per sq. cm. (approximately 3 to 50 pounds per square inch), a range considerably below that of most vulcanized stocks. These limits can be exceeded by employing films of large or very small cross-section, as the case may be, but, in general, the above values define the working range. When it is considered that the 10-minute constant-stress modulus of unmilled pale natural crepe is in the range of 2 to 3 megadynes per sq. cm. (29 to 43 pounds per square inch), it is obvious that the method can be applied to very soft compounds.

Because of the inertia of the load, this test, or any test in which the load is applied from rest, does not permit the measurement of an instantaneous elongation. In addition, the early elongation is further complicated by oscillations which are set up when the bob is dropped into the water, and these oscillations persist for a fraction of a second before they are damped out. Although a mathematical analysis does permit a calculation of an earlier modulus, it has been most practical to take the first measurement at 0.01 minute, where a reasonably steady state is realized.

ANALYSIS OF CREEP CURVES

At the outset, a few elastomers were subjected to constant-stress elongation over time periods of 24 hours or more. Curves of elongation *vs.* time for four of the materials—natural rubber, polyethyl acrylate, polymethyl acrylate, and polyvinyl acetate—are shown in Figure 3.

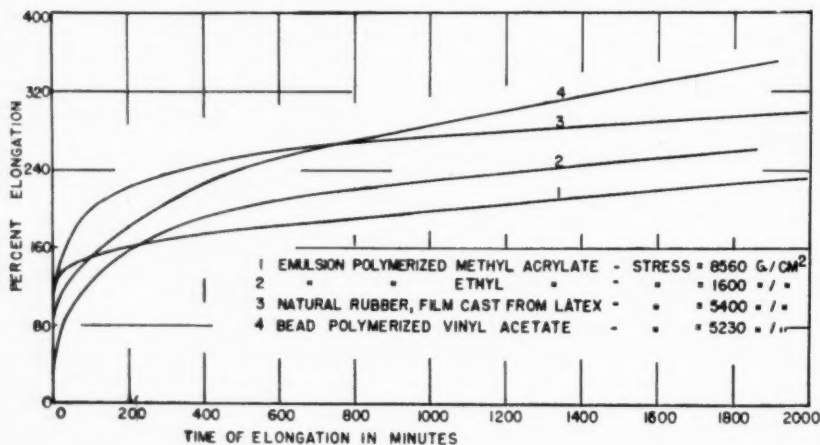


Fig. 3.—Elongation of polymeric films at constant stress.

These curves were analyzed by the method used by Taylor in his treatment of the creep curves of glasses¹. Resolving the total deformation into three components: (1) instantaneous elastic elongation; (2) delayed elastic elongation; and (3) viscous flow, Taylor has shown that the creep curve of soda glass near

the annealing temperature can be represented fairly well by the sum of the three processes as follows:

$$E_t = I + L_1(1 - e^{-kt}) + k_v t$$

where E_t = over-all elongation at time t
 I = instantaneous elastic elongation
 L_1 = total delayed elastic elongation
 e = base of natural logarithms
 k = rate constant for the delayed elastic process
 t = time
 k_v = constant rate of viscous flow.

DISCUSSION OF CREEP AND RECOVERY DATA

When equations of this type were fitted to the creep curves of polymers, it became evident that the viscoelastic behavior was considerably more complex than that of soda glasses. The delayed elastic elongation could not be represented by one or two elements of the type $L_1(1 - e^{-kt})$, but at least four, and in some cases more than six, were required. Taylor showed that at least two such terms were necessary for potash glasses. It has been pointed out by Alfrey⁶ that the geometry of creep curves is such that the delayed elasticity can be closely approximated with a few such elements, but each of these is in turn an approximation of several others having roughly the same relaxation times. Consequently, a more plausible concept of the relaxation mechanism is that of a very large number of delayed elastic processes and a whole spectrum of relaxation times.

Taylor's concept of viscoelastic deformation in glasses represents the purely viscous deformation as a flow rate which is proportional to the stress and independent of the strain. The rate of viscous flow is obtained from the slope of the creep curve after the delayed elastic deformation is essentially complete, and the magnitude of the viscous deformation can be obtained from the product of the final slope of the curve and the deformation time.

In the extended time range, the creep curves of Figure 3 appear to have attained a constant slope. The viscous deformation as calculated from the final slope and the deformation time is compared in Table I with the observed set after a 60-day recovery period. It is seen that the calculated viscous flow agrees fairly well with the observed set in the case of natural rubber and polyethyl acrylate, whereas the polymethyl acrylate and polyvinyl acetate films show no agreement between observed and calculated values. Furthermore, the natural rubber and polyethyl acrylate films, when placed in an oven at 100° C, displayed additional rapid recovery, indicating that the agreement between observed and calculated set was probably fortuitous. The deformation of polymethyl acrylate and polyvinyl acetate in the extended time range is in reality a highly delayed elastic process, with a relaxation time so great that the creep resembles viscous flow.

While the rate constant for viscous flow may be invariant over the entire deformation time range in the case of some glasses, it is questionable that the same holds true for materials as deformable as the soft polymers. Intermolecular attraction may increase considerably as a result of orientation during stretching. For example, the viscosity of natural rubber at small strains may be lower than the viscosity in the crystalline state which obtains at high elongation.

TABLE I
CONSTANT-STRESS ELONGATION AND RECOVERY OF ELASTOMERS
(Temperature 25° C)

	Polyvinyl acetate (Bead polymer film cast from solution)		Polymethyl acrylate (Emulsion polymer, film cast from solution)		Polyethyl acrylate (Emulsion polymer, film cast from latex)		Natural rubber (Latex film)	
	Stress (kg./sq. cm.)							
	5.25		8.56		1.60		5.40	
Time (min.)	Deformation (cm.)	Modu- lus	Deformation (cm.)	Modu- lus	Deformation (cm.)	Modu- lus	Deformation (cm.)	Modu- lus
0.01	—	—	—	—	0.62	7.59	1.95	8.15
0.02	—	—	—	—	0.64	7.35	2.08	7.64
0.1	0.33	46.8	1.49	16.9	0.71	6.62	2.43	6.53
1.0	1.35	11.4	2.83	8.9	0.89	5.29	2.94	5.40
10	2.74	5.64	3.73	6.76	1.32	3.56	3.94	4.03
100	4.54	3.40	4.53	5.56	3.25	1.45	5.92	2.68
1,000	8.85	1.75	6.13	4.11	6.88	0.68	8.34	1.90
1,600	9.86	1.57	—	—	7.61	0.62	—	—
7,000	—	—	7.99	3.16	—	—	—	—
10,000	—	—	—	—	—	—	10.70	1.48
13,000	—	—	—	—	—	—	11.23	1.41
Time after release (min.)	Deformation (cm.)	Recovery (%)	Deformation (cm.)	Recovery (%)	Deformation (cm.)	Recovery (%)	Deformation (cm.)	Recovery (%)
0.1	9.00	8.7	5.31	33.5	6.12	19.5	7.10	36.9
1	7.04	28.6	3.32	58.4	5.49	27.9	6.56	42.2
10	4.91	50.1	2.37	70.3	4.84	36.4	5.75	48.9
100	3.36	65.9	1.72	78.5	3.73	51.0	4.67	58.5
1,000	2.04	79.3	1.07	86.6	2.60	65.8	3.60	68.0
10,000	0.80	91.9	0.56	93.0	2.05	73.0	2.47	78.0
100,000	0.19	98.1	0.02	99.7	1.50	80.3	1.33	88.2
Ultimate recovery calculated from final slope of creep curve	3.33	66.2	0.90	88.7	1.79	76.5	1.26	88.8

Modulus value (megadynes per sq. cm.) are calculated on basis that all of deformation is elastic.

Recovery resembles reverse creep to the extent that it is initially rapid, but always decreasing in rate (Figure 4). While recovery persists for a much longer time than the time of elongation, it is related to the time of elongation in that its duration depends on the elongation time. Thus, films stretched for 10 minutes recover in 1 or 2 days, while films stretched for 24 hours may require a month or more to recover.

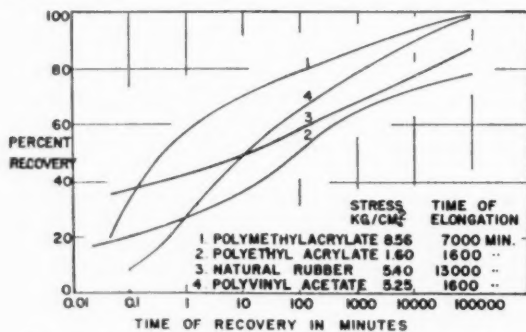


FIG. 4.—Recovery of elastomers after constant-stress elongation.

Hopes of obtaining appreciable permanent set by employing high stresses did not materialize, owing to localized flow in the films (necking down). Apparently it is difficult to effect uniform viscous flow in a strip of soft polymer. In view of the foregoing, efforts to utilize the test for viscosity measurements were abandoned. Suffice it to say that the viscous deformation is usually a very minor part of the total deformation when the stress is such that an elongation of no more than 500 per cent is realized in 10 minutes. If there should be appreciable viscous flow due to excessive plasticizer content or low average molecular weight, it almost invariably results in film failure.

In Figure 5, a semilogarithmic plot of the creep curves of Figure 3 illustrates the short-time elastic behavior of the polymers. The curves of Figure 3 indicate considerable similarity in the highly delayed elasticity of these materials, but Figure 5 brings out distinct dissimilarities in the short-time elasticity.

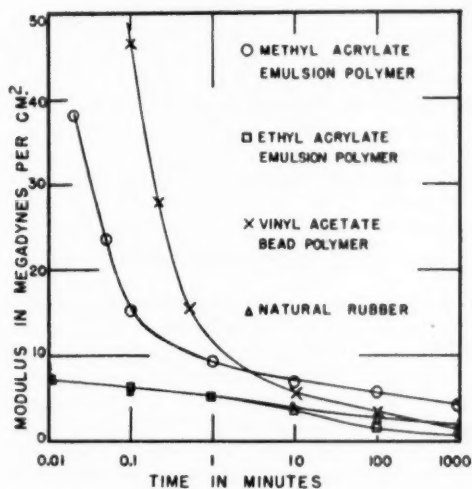


Fig. 5.—Change in modulus with time at constant stress.

Here the stiff, nonrubbery polyvinyl acetate and polymethyl acrylate show high moduli at short elongation times, while natural rubber and polyethyl acrylate offer much less resistance to quick stretching.

The modulus, G_t , is defined as follows:

$$G_t = \frac{\text{stress} \times \text{initial length}}{\text{deformation at time } t}$$

It is obvious that G_t will decrease as long as the film continues to stretch, *i.e.*, as long as relaxation occurs. The drop in G_t does not, however, indicate a decrease in the intermolecular attractive forces. Because G_t is not measured under static conditions, there is continual breaking and reforming of the intermolecular (and to some extent, intramolecular) bonds. These may result from polar attraction, hydrogen bonding, van der Waals forces, or mechanical entanglement of long molecules. Under constant stress the rate of elongation is observed to decrease with time, indicating that the stress is continually shifting

to stronger and stronger bonds. The rate of decrease in G_t varies inversely with the rate at which the intermolecular attractive forces are increasing.

Because of a lack of strong intermolecular forces, the initial uncoiling and straightening of the rubber molecules are relatively unhindered. However, as the chain segments are extended and brought into alignment, localized crystallization begins and the stress is then shifted to very strong bonds.

In polyvinyl acetate and polymethyl acrylate the chain segment motion is hindered by strong polar attraction and, consequently, the short-time modulus is much higher than for natural rubber. Again the stress shifts to stronger bonds, but intermolecular attractive forces now are approximately the same as in extended rubber, and at long elongation time the moduli of polyvinyl acetate or polymethyl acrylate approach the moduli of natural rubber. It is of interest also that these stiff polymers are compatible of the same high extension as natural rubber.

Apparently the polar groups of polyethyl acrylate are so masked by the ethyl groups that they cannot approach each other, and the reduced interaction between chain segments permits considerable freedom of motion. In the time range of 0.01 to 10 minutes, the moduli of polyethyl acrylate are of the same order of magnitude as the moduli of natural rubber, but at higher elongation time the moduli of polyethyl acrylate fall below those of natural rubber.

The curves of Figure 5 indicate very clearly the importance of the time element in the elastic behavior of polymers. At 0.1 minute the modulus of the polyvinyl acetate is about three times that of the polymethyl acrylate and about eight times that of natural rubber, but at 400 minutes the polyvinyl acetate modulus is equal to that of natural rubber and only one-half that of the polymethyl acrylate.

The importance of the time element is illustrated in a different manner in Table II. Here GR-S-50 and a low molecular-weight fraction of the same rubber were tested at constant stress and at constantly increasing load. The latter test, conducted on a commercial inclined-plane machine, failed to show any difference in the elastic properties of the two samples. Under constant stress elongation, the moduli of both rubbers were of the same order of magnitude in the range 0.01 to 0.1 minute. However, at longer time the modulus-time curve of the low molecular-weight fraction fell below that of the unfractionated GR-S. Although the low molecular weight fraction failed before the completion of a 10-minute test, it is indicated by the 24-hour recovery (96 per cent) that viscous flow contributed very little to the total deformation. Failure of the inclined-plane tester to reveal a difference in the elastic properties is due to the fact that it completed the elongation within 0.1 minute.

The inherent viscosities of the two rubbers indicate a 2- to 2.5-fold difference in viscosity average molecular weight, and the approximate range of molecular weight, calculated from the relationship⁷: $[\eta] = 5.25 \times 10^{-4} M^{0.667}$, is 100,000 to 300,000. The two rubbers are almost identical in their short-time elastic response, i.e., response at time intervals shorter than 0.1 minute. The elastic behavior in this time range is evidently independent of molecular weight, at least within the range of 100,000 to 300,000, and, therefore, must be concerned with displacements of relatively short segments of the molecules. The highly delayed elastic response, which is very different for the two rubbers, is concerned with uncoiling of segments of such length that resistance to segment motion depends on chain length.

The Mooney values of the above rubber samples were 34 for the low molecular-weight fraction, and 49 for the unfractionated rubber. It is of some interest

TABLE II

ELONGATION OF STANDARD GR-S-50 AND LOW MOLECULAR-WEIGHT FRACTION OF GR-S-50 AT CONSTANT STRESS AND CONSTANTLY INCREASING LOAD

Modulus <i>vs.</i> Time at Constant Stress					
Standard GR-S-50. Stress = 2.5 kg. per sq. cm.					
Time (min.)	0.01	0.1	1	10	30
Elongation (%)	39.2	77.6	159	275	342
Modulus (megadynes/sq. cm.)	6.25	3.16	1.54	0.89	0.72
Time of recovery (min.)	0.1	1	10	60	1440
Recovery (%)	49	67.5	83.5	92	97
Low molecular-weight fraction of GR-S-50. Stress = 1.7 kg. per sq. cm.					
Time (min.)	0.01	0.1	1	10	
Elongation (%)	27.2	65.6	192	Failed, 2.5 min.	
Modulus (megadynes/sq. cm.)	6.13	2.54	0.87	—	
Time of recovery (min.)	0.1	1	10	60	1440
Recovery (%)	—	70	87.5	93.5	96
Modulus <i>vs.</i> Elongation at Constantly Increasing Load					
Standard GR-S-50					
Elongation (%)	20	50	100	300	800
Stress (kg./sq. cm., final cross-section)	1.00	2.04	3.57	9.18	24.5
Modulus (megadynes/sq. cm.)	4.9	4.0	3.5	3.0	3.0
Time of elongation (min.)	0.03	0.05	0.066	0.085	0.10
24-hour recovery = 99%					
Low molecular-weight fraction of GR-S-50					
Elongation (%)	20	50	100	300	800
Stress (kg./sq. cm., final cross-section)	1.02	2.04	3.57	9.18	23.7
Modulus (megadynes/sq. cm.)	5.0	4.0	3.5	3.0	2.9
Time of elongation (min.)	0.03	0.05	0.065	0.084	0.096
24-hour recovery = 98%					
Inherent viscosities (0.1%, benzene)	GR-S-50	2.34			
	Fraction	1.32			
Temperature 25° C					

that 10-minute constant-stress moduli generally increase with the Mooney plasticity, although the former is a measure of resistance to elastic deformation and the latter a measure of viscosity. The constant-stress method can be used to good advantage in characterizing gum stocks in terms of fundamental elastic constants and should be of value in the rubber industry.

CONSTANT-STRESS ELONGATION OF COMMERCIAL GUM RUBBERS

To make the test a practical one, it is necessary to set a limit on the time of elongation, and experience indicates that a 10-minute period is adequate for most purposes. Results of such tests on commercial gum rubbers are shown in Figure 6 and Table III. To express the elastic behavior as briefly as possible, the two reference times of 0.01 and 10 minutes have been chosen, and the elastic properties are given in terms of the 10-minute modulus and the ratio of the 0.01-minute modulus to the 10-minute modulus. It is obvious from Figure 6 that two values do not give a complete picture of the elastic behavior of Hycar OR-25 and the GR-S rubbers. On the other hand, natural rubber, Vistanex B120 and Hycar-PA, which show an almost linear relation between modulus and log time, can be characterized fairly well by the two modulus values.

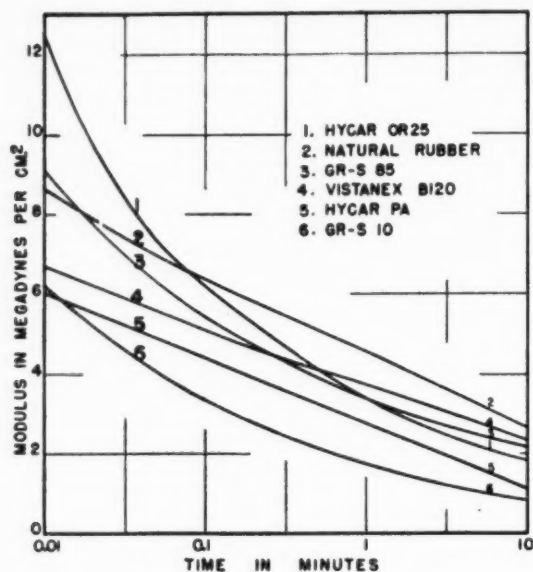


Fig. 6.—Modulus-time curves of gum rubbers.

The low modulus ratios of Vistanex and natural rubber are apparently due to crystallization at high elongation⁸. The molecular configuration of these polymers is such that adjacent chain segments can fit into a crystal lattice when suitably oriented by stretching. Crystallization has the effect of a cross-linking reaction binding the amorphous portions of the polymer into a network. As crystallization proceeds, the remaining amorphous chain segments become increasingly constrained in movement, and the rate of elongation under constant stress decreases rapidly. The result is that the change in modulus with time becomes relatively small, and therefore the ratio of the 0.01-minute modulus to the 10-minute modulus is low.

High gel content, which is a result of chemical cross-linking, has a similar effect on the modulus ratio. GR-S-85, which has a gel content of 60 to 65 per

TABLE III
ELASTIC PROPERTIES OF COMMERCIAL GUM RUBBERS ELONGATED
AT CONSTANT STRESS

	Stress (kg./sq. cm.)	Total elonga- tion time (min.)	G_{10} Min. (25° C)	$\frac{G_{0.01} \text{ Min.}}{G_{10} \text{ Min.}}$	Recovery (%)	
					10 min.	24 hours
Natural rubber	3.1	30	2.7	3.2	73	92
GR-S-10	1.3	20	0.85	7.3	81	97
GR-S-85	2.9	20	2.2	4.1	86	98
Hycar OR-25	3.1	20	1.9	6.6	83.5	99
Hycar-PA	2.35	20	1.1	5.3	75.5	95
Vistanex B120	2.5	20	2.3	2.9	79.5	95

Modulus values in megadynes per sq. cm. All films cast from solution. Natural rubber unmilled, others milled 10 minutes on cold mill before preparation of solution.

cent, shows a much lower modulus ratio than GR-S10, which has less than 5 per cent gel. These rubbers do not crystallize on stretching.

Creep curves can be obtained at various temperatures by enclosing the test sample and blowing in cooled or heated air. No extensive modulus-temperature studies have been made on uncompounded gum rubbers, but a few measurements have been taken on natural rubber and GR-S-10. The data (see Figure 7) indicate that the temperature dependence of modulus is greater the longer the time of elongation, *i.e.*, the relative change in the 0.01-minute modulus with temperature is less than the relative change in the 10-minute modulus.

The question may arise: Under constant-stress conditions, is the elongation at a specified time directly proportional to the stress? In other words, are the

TABLE IV
DEFORMATION OF PLASTICIZED ACRYLONITRILE RUBBER COMPOUND
UNDER DIFFERENT STRESS CONDITIONS

	A	B
Initial length, L_0 (cm.)	3.04	3.02
Initial width (cm.)	0.275	0.575
Initial thickness (cm.)	0.084	0.077
Initial load (grams)	50.0	50.0
Temperature ($^{\circ}$ C)	25	25

Modulus, Stress Based on Final Cross-Section

Stress = 2160 grams/sq. cm.			Stress = 1130 grams/sq. cm.		
Time (min.)	Deformation (cm.)	Modulus	Time (min.)	Deformation (cm.)	Modulus
0.01	1.81	3.56	0.01	0.94	3.56
0.1	4.15	1.55	0.1	2.00	1.67
1.0	13.48	0.48	1.0	6.39	0.52
10.0	31.50	0.204	10.0	17.15	0.195

Modulus, Stress Based on Original Cross-Section

Time (min.)	Deformation (cm.)	Stress (g./sq. cm.)	Modulus	Time (min.)	Deformation (cm.)	Stress (g./sq. cm.)	Modulus
0	0	2160	—	0	0	1130	—
0.01	1.81	1354	2.23	0.01	0.94	862	2.72
0.1	4.15	914	0.656	0.1	2.00	680	1.01
1.0	13.48	398	0.088	1.0	6.39	362	0.168
10.0	31.50	190	0.018	10.0	17.15	169	0.029

$$\text{Modulus} = \frac{\text{stress} \times L_0 \times g}{\text{Deformation} \times 10^6} \text{ megadynes per sq. cm.}$$

g = acceleration of gravity

0.01-minute modulus and the 10-minute modulus independent of stress? It has been found that the moduli of soft elastomers, particularly the highly plasticized gum compounds, are independent of stress, provided the deformation does not approach the elastic limit, and there is no reinforcement due to crystallization such as occurs in natural rubber and Butyl-rubber compounds. The moduli of plasticized butadiene-styrene or butadiene-acrylonitrile rubbers are independent of stress over a wide range. It will be observed in Table IV that the modulus values of a plasticized acrylonitrile rubber are in excellent agreement, although the stress value is almost doubled.

The above statements hold only when the moduli are calculated from stress values based on the cross-sectional area of the stretched film. If, as shown in

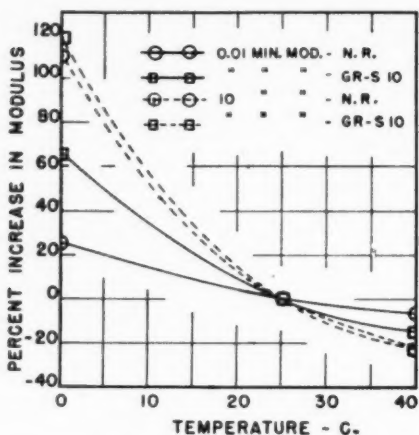


Fig. 7.—Temperature dependence of 0.01-minute and 10-minute constant-stress moduli of natural rubber and GR-S-10.

Table IV, the stress is based on the original cross section, the modulus values are not in agreement and, therefore, cannot be used as a basis for comparing elastic properties.

APPLICATION OF CONSTANT-STRESS TO EVALUATION OF RUBBER PLASTICIZERS

The 0.01-minute constant-stress modulus serves as a measure of the flexibility, as indicated by the low 0.01-minute modulus of the very flexible natural rubber film and the high 0.01-minute modulus of the stiff polymethyl acrylate film (Figure 3). The internal strength can be estimated from constant-stress modulus values by consideration of two factors: (1) the magnitude of the modulus at some specified time in the extended time range, and (2) the rate of change in modulus with time. (Tensile tests are of no value because highly plasticized polymers flow under high stress and do not show any definite breaking points.) The 10-minute modulus, and the ratio of the 0.01-minute modulus to the 10-minute modulus, serve, respectively, to evaluate these factors. If the 10-minute modulus is low (<0.3 megadyne per sq. cm.) and the modulus ratio high (>10), the polymer has low internal strength. An example would be a highly plasticized natural-rubber compound which had undergone excessive milling. A low 10-minute modulus (0.3 to 0.7 megadyne per sq. cm.) together with a low modulus ratio (2 to 6) denotes a very soft polymer which tensilizes (exhibits "nerve") on stretching. Highly plasticized unmilled natural rubber exemplifies such a material. A strong, rubbery polymer, such as unmilled natural rubber, has a relatively high 10-minute modulus (1.5 to 3 megadynes per sq. cm.) and low modulus ratio (2 to 6), while a firm, stiff polymer such as polymethyl acrylate is characterized by high modulus values (10-minute modulus >3 megadynes per sq. cm., 0.01-minute modulus >20 megadynes per sq. cm.), the modulus ratio indicating whether the internal strength is high (ratio <6) or low (ratio >10).

A rather extensive study has been made of the elastic properties of Hycar OR 25-plasticizer blends. The purpose of adding plasticizer was to improve

the "quick stretch" or rubberiness, and it was desired to accomplish this with a minimum loss in internal strength. In terms of the constant-stress data this means that it was desired to decrease the 0.01-minute modulus at a minimum expense to the 10-minute modulus, or, in deference to the proposal that the 10-minute modulus and modulus ratio serve as the criteria of elastic properties, it would mean a maximum decrease in modulus ratio for a minimum decrease in the 10-minute modulus. Actually it was observed experimentally that the 10-minute modulus in almost all cases decreased relatively more than the 0.01-minute modulus, so the modulus ratio usually increased, and the best which could be hoped for was a minimum increase in the modulus ratio for a given lowering of the 10-minute modulus.

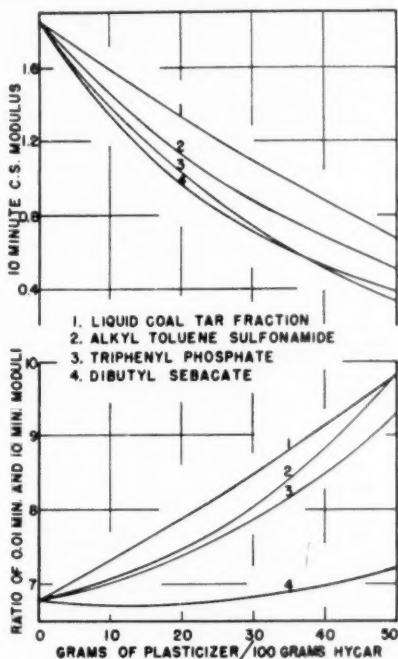


FIG. 8.—Elastic properties of plasticized Hycar OR-25.

Figure 8 shows the change in elastic properties of Hycar OR-25 with plasticizer content in the range of 0 to 50 parts per 100 parts of rubber (by weight). Four plasticizers which give a rather wide spread in elastic properties were selected. Triphenyl phosphate and dibutyl sebacate are almost equivalent with respect to effect on 10-minute modulus, but the modulus ratio undergoes a pronounced increase with triphenyl phosphate and is relatively unchanged with dibutyl sebacate. Therefore dibutyl sebacate imparts more "quick stretch" or flexibility, with less sacrifice of internal strength.

The liquid coal-tar fraction and the alkyltoluene sulfonamide do not reduce the 10-minute modulus to the same degree as do triphenyl phosphate or dibutyl sebacate, but effect a greater increase in the modulus ratio. To gain an equiv-

alent increase in quick stretch, it is necessary to use a higher percentage of these plasticizers, with consequent loss in internal strength. Of the four, dibutyl sebacate is the preferred plasticizer on the basis of these measurements. Other factors, such as low temperature performance and volatility, must also be considered.

SUMMARY

The elastic properties of polymeric materials which are too soft to test on conventional stress-strain machines can be obtained by elongation at constant stress. A simple apparatus has been developed for maintaining constant stress during elongation.

Data illustrate the time dependence of the elastic behavior of polymeric materials and demonstrate the usefulness of the constant-stress method in the evaluation of this time dependence. The constant-stress method is useful in the evaluation of plasticizers for gum rubbers.

Because of the difficulty of separating highly delayed elastic elongation from viscous flow, the method has not been found practical as a tool for measurement of viscosity in the solid state. However, under most test conditions, viscous flow has been a negligible fraction of the total deformation.

Several terms for delayed elasticity are required to fit an empirical equation to the elongation-time curves, and it seems probable that these terms are only an approximation of a very large number of delayed elastic processes having different relaxation times.

ACKNOWLEDGMENT

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EFFECT OF STORAGE OF MILLED RUBBER ON ITS MOLECULAR WEIGHT *

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It is important to know whether the molecular weight of milled rubber alters on storage. The results hitherto reported¹ have been contradictory, possibly due to oxidation occurring during storage.² The answer was sought by measuring the solution viscosity of stored milled rubber.

SOLUTION VISCOSITY

Solution viscosities were determined by placing 1-gram samples of rubber in 50 cc. of Analar benzene in a conical flask. Nitrogen, purified by passage through alkaline pyrogallol solution and then concentrated sulfuric acid, was passed through the liquid for ten minutes. The flasks were then corked and placed in a thermostat at 24.7 to 25.0° C until the rubber dissolved. Twenty cc. of the solution was pipetted into an Ostwald viscometer, kept in the same thermostat. The average of five times of fall between the marks was determined: they agreed within 0.2 second.

The same viscometer was used throughout. Between measurements on different solutions it was cleaned with potassium dichromate and sulfuric acid, followed by distilled water, and finally ether.

PLASTICITY

Plasticities of the milled rubbers were initially determined by compressing 2-gram rubber samples in a Williams plastometer for 3 minutes under a load of 5 kilograms at 70° C, after a 15-minute preheating. The heating at 70° C destroyed the crystalline structure which obviously developed in many of the masticated samples during storage. These results are, therefore, not recorded. In an attempt to record more accurately the initial plasticity of these samples, later measurements were made by compressing 0.5-gram samples for 3 minutes under a 5-kilogram load at room temperature. Cigarette paper was used to prevent the pellets sticking to the plastometer plates.

MILLING AND STORAGE

Lots of 110 grams of pale crepe were masticated on a 9-inch mill for 13 and 23 minutes. Water was flowing through both rolls, which were running at a friction ratio of 2:1. Milling began with the rolls at 15° C.

Lots of 110 grams of pale crepe were masticated on the same mill for 7 and 17 minutes, respectively, with steam passing through both rolls. The rolls were at 75° C initially.

* Reprinted from the *India-Rubber Journal*, Vol. 120, No. 23, pages 919-920, June 9, 1951.

TABLE I
COLD MILLED RUBBER—PLASTICITY AFTER STORAGE

Time of storage (day)	Temperature of determination (° C)	Height in plastometer (1/100 mm.)	
		Milled 13 min.	Milled 23 min.
6.0	20	340	254
7.0	18	356	243
8.0	14	362	294
10.2	13	346	285
13.2	12	400 (a)	292 (a)
17.0	16	340	302
22.2	18	432 (b)	390 (b)
22.3	18	383 (c)	290 (c)
23.5	20	347	300

TABLE II
COLD MILLED RUBBER—SOLUTION VISCOSITY AFTER STORAGE

Time of storage (day)	Temperature of thermostat (° C)	Time of fall (sec.)	
		Milled 13 min.	Milled 23 min.
0.0	24.8	54.5	20.6
1.0	24.8	55.3	21.7
2.0	24.7	54.2	20.5
3.0	24.7	55.7	21.2
8.0	24.7	54.8	21.2
15.0	24.9	54.5	21.2
23.0	24.9	54.1 (d)	21.1 (d)

TABLE III
HOT MILLED RUBBER—PLASTICITY AFTER STORAGE

Time of storage (day)	Temperature of determination (° C)	Height in plastometer (1/100 mm.)	
		Milled 7 min.	Milled 17 min.
0.7	18	343	265
1.7	14	375	301
3.9	13	370	290
6.8	12	368	296
10.8	16	348	280
15.8	18	350 (b)	320 (b)
15.9	18	346 (c)	294 (c)
17.0	20	347	275

TABLE IV
HOT MILLED RUBBER—SOLUTION VISCOSITY AFTER STORAGE

Time of storage (day)	Temperature of thermostat (° C)	Time of fall (sec.)	
		Milled 7 min.	Milled 17 min.
0.7	24.7	141.3	58.7
2.7	24.7	136.1	58.2
3.7	25.0	138.1	59.5
9.7	25.0	132.1	58.7
16.7	25.0	140.9 (d)	58.3 (d)

The milled rubber was allowed to stand at room temperature in the dark in a desiccator (no desiccant) with two openings. A current of purified nitrogen was passed through the desiccator for 10 minutes at least twice a day to prevent surface oxidation of the rubber.

The values of the "plasticity" and the solution viscosity of milled rubber stored for varying periods are given in Tables I, II, III, and IV.

NOTES

(1) The rubber had been left over a week-end, and both samples were opalescent and hard. That milled for 23 minutes was harder than that milled for 13 minutes. Both samples softened on being cut to get the 0.5-gram sample.

(2) and (3). Two samples of each rubber were weighed out for a plasticity determination and were cooled with solid carbon dioxide for five hours. The height of one sample (b) was determined immediately. The compression seemed to thaw the samples. The other sample (c) was allowed to stand at room temperature for 40 minutes between being removed from the cooling bath and being placed in the plastometer.

(4) The rubber samples were weighed for viscosity determinations, cut up, and placed in flasks. Nitrogen was passed through the flasks, which were then corked. They were cooled with solid carbon dioxide for 24 hours, after which benzene was added and the viscosity of the resulting solution determined in the usual way.

Initial variations in the height of the pellets caused variations in the height found in the plastometer after 3 minutes. The variations in viscosity were probably due to loss of benzene as spray on the passage of nitrogen.

The hot milled samples took longer to harden than the cold milled ones. The former also seemed easier to thaw.

CONCLUSION

No significant difference was observed between the viscosities of solutions made from milled rubber stored for varying periods.

Some crystallization of the milled rubber had occurred, but this did not affect the solution viscosity. The plasticity measurements on the samples cooled with solid carbon dioxide confirm this hardening, but it is apparently an effect unconnected with change in molecular weight.

ACKNOWLEDGMENTS

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THE ACTION OF UNSATURATED COMPOUNDS ON NATURAL RUBBER IN SOLUTION

I. THE REACTION CATALYZED BY A PEROXIDE *

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By virtue of its hydrocarbon character, natural raw rubber is soluble in both aliphatic and aromatic hydrocarbons. However, when a three-dimensional structure is set up by vulcanization, the rubber no longer dissolves, but simply increases in volume by absorbing liquid to an extent which depends on the type of rubber mixture concerned.

This property, termed swelling, is a serious disadvantage of vulcanized rubber, for in this process it loses practically all of its toughness. As a result, natural rubber products in most cases become useless when they are in contact with a hydrocarbon or a fatty material. On the contrary, some of the synthetic elastomers, notably the Perbunans, show remarkable resistance to the action of substances which are deleterious to natural rubber.

Beginning in 1940, the French Rubber Institute undertook to find a method of modifying natural rubber chemically with a view to offsetting this serious fault. The initial experiments carried out with this end in view took advantage of work by previous investigators who had already studied this problem and who had shown that it is possible to combine rubber with acrylonitrile, even when the rubber is in latex form. It had been known, in fact, that cyanide groups diminish the affinity of high polymers for solvents, as is true, for example, of Perbunan. The results which were obtained were encouraging, but the mechanical properties of the products were unsatisfactory, and it was evident at once that the reaction was very complex. In addition, the problem arose as to the mechanism of such a transformation and what is the structure of the products when ethylenic derivatives of acrylonitrile are used (as a general rule, it is necessary to avoid the use of acrylonitrile because of the processing difficulties which are encountered).

PREVIOUS INVESTIGATIONS PERTAINING TO THE PROBLEM

In 1938, Bacon, Farmer, and Schidrowitz¹, and later in 1939 Bacon and Schidrowitz², described mixtures of rubber with different vinyl polymers such as polyacrylonitrile, polystyrene, and certain polymethacrylates. These investigators added to natural-rubber latex synthetic latexes of these polymers and then coagulated the mixtures. However, their experiments were inconclusive, and in 1940, Twiss, Neale, and Hale³ confirmed the difficulties which are encountered when an attempt is made to polymerize a vinyl monomer in latex form or even in a solution of rubber.

These investigators likewise tried to combine unsaturated compounds with rubber by the action of sulfuric acid, but the results obtained were disappointing.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 26, No. 6, pages 426-432, June 1949. This paper was presented at the 11th International Congress of Pure and Applied Chemistry in London, July 1947. It comprises extracts from an engineering doctorate thesis, prepared at the French Rubber Institute, and submitted at Paris, June 5, 1947.

Nevertheless, combination of rubber with unsaturated compounds was found to be possible, for in 1938 Bacon and Farmer⁴ reported such a combination with maleic anhydride. These investigators employed dilute solutions of rubber in toluene, which they refluxed with maleic anhydride and with benzoyl peroxide as catalyst of the reaction. By measuring the increase of weight of the rubber, they found that the proportion of maleic anhydride which combines depends on the initial proportions of benzoyl peroxide and maleic anhydride. They observed also that, with a concentration of rubber greater than 3-5 per cent, gelation usually occurs. Finally, they established the fact that, for each molecule of maleic anhydride which unites with the rubber, there is a reduction of one double bond of the rubber.

This work of Bacon and Farmer was the starting point of investigations in this field carried out by the French Rubber Institute, investigations which at the beginning were based on the following considerations.

Some synthetic elastomers which contain $C\equiv N$ groups have good mechanical properties, high elasticity, and very little tendency to swell in solvents. According to Bacon and Farmer, it is possible to make rubber combine with an active unsaturated compound such as maleic anhydride, so it seemed also possible that other active ethylenic compounds which at the same time carry $C\equiv N$ groups, *e.g.*, acrylonitrile, would likewise combine with rubber.

In 1941 Compagnon and Le Bras⁵ showed the possibility of fixing certain vinyl monomers to raw rubber in the solid state, or when dispersed, as in the latex form, for example.

When solid rubber is mixed with maleic anhydride on a cold mill having corrugated rolls, it is not necessary to add a catalyst for the characteristic reaction to take place⁶. The rubber unites with the maleic anhydride and is transformed into a product which has almost no elasticity and is insoluble in ordinary solvents. A similar reaction takes place with maleic imide containing no substituents and with maleic imide derivatives containing nitrogen-substituted alkyl radicals⁷.

By carrying out the reaction in emulsion with acrylonitrile in the presence of a catalyst like benzoyl peroxide, it is possible to modify rubber chemically when in the latex form itself. After coagulation and drying, the modified rubber can be mixed with standard compounding ingredients and can then be vulcanized. The vulcanizates show a notably low tendency to swell in solvents, but at the same time relatively poor mechanical properties, in particular their elasticity⁸. Le Bras and Compagnon⁹ have shown that the products are not mixtures of rubber and polyacrylonitrile, but rather compounds of rubber and monomeric acrylonitrile.

The reaction in emulsion offers a number of advantages, but, as has been pointed out, the products give vulcanizates which, although resistant to solvents, have relatively poor elasticity.

Consequently, because of the complex nature of the reaction mixture, it was decided to make a systematic study of the factors involved in the fixation of an ethylenic compound by changing one factor at a time, but this time in solution, *i.e.*, in a homogeneous phase.

EXPERIMENTAL TECHNIQUE

Bacon and Farmer⁴ carried out their experiments with solutions of rubber in toluene, which they refluxed without taking any special precautions. Repeating the experiments of these investigators, the present author observed that

atmospheric oxygen causes a more or less pronounced degradation of the rubber during the reaction¹⁰, a phenomenon to which attention has already been called by Shimada¹¹.

Since, in these experiments, it was impossible to control this action of oxygen, a special technique had to be developed whereby it was possible to operate in the complete absence of air. In doing this, advantage was taken of the method which Moureu and Dufraisse¹² had employed in their investigations of the autoxidation of acrolein. The principle is to carry out the reaction in a sealed glass tube containing the rubber and the different reagents and into which, after having set up a vacuum of 0.001 mm., the solvent (in most cases pure benzene) has been introduced and freed to the highest degree possible of oxygen.

After having been sealed, the tube is heated for a predetermined length of time at the chosen temperature. This procedure has an advantage over that of Bacon and Farmer in that it is possible, if desired, to operate at temperatures higher than that of the boiling point of the solvent.

After heating and cooling, the modified rubber is precipitated from its solution by methanol, is then washed with methanol, dried roughly, redissolved in benzene, precipitated a second time by methanol, and finally dried in a vacuum for several days. This method of purification is sufficient to eliminate completely any of the reagents which have not reacted. The products of the reaction are then analyzed.

The rubber used in the experiments was pale crepe which had been extracted with acetone and precipitated from a solution in petroleum ether by anhydrous alcohol. In most cases only 0.5 gram of rubber was used, so for each individual test it was necessary to employ methods of analysis in the determination of nitrogen, bromine, and iodine number which were applicable to samples of only 0.05-1 gram. For the determination of bromine, the method described by Willard and Thompson¹⁴ for incinerating the sample is well suited; the bromine ions which are formed are then determined potentiometrically. In this way it is possible to measure, with a precision of 1 per cent, up to 2 per cent of bromine in a sample weighing 0.1 gram.

GELATION

In efforts to explain the structure of the addition products of rubber and unsaturated compounds which were studied, it was of importance to determine, by their iodine numbers, their degrees of unsaturation. To this end, it was necessary that the products be soluble, and, in addition, to operate under conditions, particularly with respect to temperature and concentration of rubber, such that the addition products did not gel. It was found that limits were rather restricted, as is evident from the following facts.

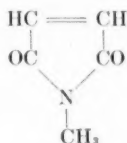
(1) In the absence of an unsaturated compound, benzoyl peroxide in proportions higher than 0.1 per cent (by weight of the rubber) in almost all cases leads to the formation of gels. This tendency to gel depends on the nature of the solvent, and the higher the temperature the less is this tendency. This gelling phenomenon should be regarded as analogous to the vulcanization of rubber by benzoyl peroxide, first described by Ostromislensky¹⁶.

(2) In the presence of an unsaturated compound, there is less tendency to gel; nevertheless, a gel forms at a temperature below 120-130° C, and also, whatever the temperature, gelation takes place if the concentration exceeds 3-4 per cent. A soluble product is obtained if the reaction is carried out at a temperature above 120-130° C, provided that the concentration is not higher than 3-4 per cent.

DETERMINATION OF THE OPERATING CONDITIONS

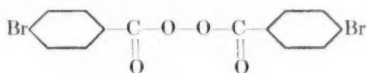
The foregoing observations make it possible to establish what operating conditions are necessary for carrying out a systematic series of experiments.

First of all, it is necessary to have a method for determining chemically the proportion of ethylenic compound which has combined with the rubber. Since the determination of combined maleic anhydride is practically impossible, it was necessary to have recourse to a compound containing an element other than carbon, hydrogen, and oxygen. The next most important element is nitrogen. The acrylonitrile unit, $\text{H}_2\text{C}:\text{CHCN}$, is easy to determine, but unfortunately this compound is liquid at ordinary temperatures and this complicates the operations. Also it is very volatile and it polymerizes very readily, so this gives a chance of erroneous results. Finally, and above all else, acrylonitrile is much less reactive than is maleic anhydride. For these reasons, nitrogen derivatives of maleic anhydride were employed in the work to be described. For various other reasons, maleic *N*-methylimide was finally selected, because



it is relatively easy to prepare, is solid at room temperature, and its reactivity with rubber is comparable to that of maleic anhydride itself.

(2) In addition to all this, it was necessary to know how benzoyl peroxide reacts during the process. To settle this question, the *p*-bromo derivative of benzoyl peroxide was chosen for study.



The presence of the bromine atoms made possible the determination, in the transformed or modified rubber, of the decomposition products of the peroxide.

It should be noted that the use of halogenated peroxides is increasing more and more; for example, Kern and Kämmerer¹⁷, Price, Kell, and Krebs¹⁸, and Bartlett and Nozaki¹⁹ have utilized them with success in their investigations of the polymerization of vinyl compounds.

(3) Finally, to obtain soluble products, benzene solutions of rubber of low concentration (3 per cent) were used in most of the work; these were heated at 130° C.

STUDY OF THE REACTION INVOLVING THE ADDITION OF MALEIC *N*-METHYLIMIDE TO RUBBER IN SOLUTION IN THE PRESENCE OF *p*-BROMOBENZOYL PEROXIDE

Three per cent solutions of rubber in benzene containing different concentrations of maleic *N*-methylimide and of *p*-bromobenzoyl peroxide from 0.5 to 50 per cent by weight of the rubber were heated for 16 hours at 130° C.

Preliminary tests had shown that the transformation products of rubber obtained in this way contain bromine. It was, therefore, necessary to explain

what grouping this bromine represents; in other words, to know what transformation *p*-bromobenzoyl peroxide undergoes during the heating. Studies of the thermal dissociation of aryl peroxides by Franck and Rabinowitch²⁰, Hey and Waters²¹, Walker and Wild²², Brown²³, Price and Kell²⁴, and McClure, Robertson, and Cuthbertson²⁵ have shown that two reactions take place, both involving the formation of free radicals. For the case of benzoyl peroxide, this process can be expressed thus: (1) $\text{H}_5\text{C}_6\text{C}(\text{:O})\text{OOC}(\text{:O})\text{C}_6\text{H}_5 \longrightarrow 2\text{C}_6\text{H}_5\text{C}(\text{:O})\text{O}^*$, and (2) $\text{H}_5\text{C}_6\text{C}(\text{:O})\text{O}^* \longrightarrow \text{C}_6\text{H}_5^* + \text{CO}_2$.

The action of benzoyl peroxide on cyclohexene has been studied by Farmer and Michael²⁶, and later by Hermans and van Eyk²⁷, and their results have confirmed the mechanism of the decomposition.

In summary, then, the foregoing facts show that, in the case of the decomposition of *p*-bromobenzoyl peroxide, there is fixation on the rubber of *p*- $\text{BrC}_6\text{H}_4\text{C}(\text{:O})\text{O}^*$ and *p*- BrC_6H_5^* free radicals, and that these latter radicals must be formed as a result of a decarboxylation reaction.

All these conclusions are based on the assumption that all of the bromine fixed on the rubber originates only from the *p*- $\text{BrC}_6\text{H}_4\text{C}(\text{:O})\text{O}^*$ free radicals.

However, this hypothesis does not conform rigorously to the actual facts, for, in the course of the experiments, the formation of very small quantities of carbon dioxide was observed, and therefore this line of reasoning evidently introduces an error in the determination of the quantity of maleic *N*-methylimide which has been fixed on the rubber.

However, it can be demonstrated by examples that this error can in most cases be disregarded. The composition of modified rubber can be expressed thus: $C + m + x = 100$, where *C* represents the rubber which has not been transformed, *m* represents the maleic *N*-methylide which is fixed, and *x* represents the decomposition products of *p*-bromobenzoyl peroxide, which have been fixed.

Let us, for example, try to determine the value of this error for a product which shows, by analysis, an *m* value of 31.5 per cent and bromine value of 1.25 per cent.

(1) If it is assumed that the bromine belongs only to *p*-bromobenzoyl groups, then $x = 3.12$, and, in this case, 100 grams of rubber which has not been transformed corresponds to a fixation of maleic *N*-methylimide:

$$M = \frac{31.5 \times 100}{100 - (31.5 + 3.12)} = 48.2\%$$

(2) If, now, it is assumed that the bromine belongs only to *p*-bromophenyl groups, $x = 2.42$, and

$$M = \frac{31.5 \times 100}{100 - (31.5 + 2.42)} = 47.7\%$$

These two values of *M*, 48.2 and 47.7, differ by only 1.04 per cent. The error calculated in this way is smaller than the maximum error for *M* (2.65 per cent) obtained in a series of ten experiments carried out with the object of verifying the reproducibility of such experiments.

If the same reasoning as before is applied to the analysis of a product containing a higher percentage of bromine, i.e., $m = 44.7$ per cent, and bromine 4.12 per cent, the following *M* values are found:

(1) assuming that the fixed bromine belongs only to *p*-bromobenzoyl groups, then $M = 99.3$ per cent.

(2) assuming that the fixed bromine belongs only to *p*-bromophenyl groups, then $M = 94.6$ per cent.

The error between these two values of M , viz., 4.7 per cent, is evidently greater than that in the first example; nevertheless, the calculation has been made for an extreme case where it is assumed that the peroxide decomposes with formation of only one kind of free radical, and this is certainly not true.

If it is assumed, for example, that more $p\text{-BrC}_6\text{H}_4^*$ radicals are fixed than are $p\text{-BrC}_6\text{H}_4\text{C}(:\text{O})\text{O}^*$ radicals, the error is reduced to about 2.5 per cent and, consequently, is still lower than the maximum error found in the series of tests concerned with the reproducibility of results.

It is obvious, then, that it is necessary to know the percentage of brominated free radicals liberated from *p*-bromobenzoyl peroxide to be able to calculate the proportion of maleic *N*-methylimide fixed by the rubber, and this calculation must be sufficiently precise.

In all these calculations, the quantities of maleic *N*-methylimide and of brominated free radicals in gram-molecules are based on the isoprene group of untransformed rubber.

If μ_0 represents the number of gram-molecules of maleic *N*-methylimide introduced per isoprene (C_5H_8) group, A_m the number of gram-molecules of *p*-bromobenzoyl peroxide introduced per isoprene group, then the number of M_m of gram-molecules of maleic *N*-methylimide fixed by one C_5H_8 group is given by the relation:

$$M = \frac{68m}{111(100 - m - p)}$$

The following table records the M_m values found for different values of A_m and of μ_0 .

<i>p</i> -Bromo- benzoyl peroxide (initial weight per 100 g. of rubber)	$A_m \times 10^3$	$\sqrt{A_m}$	$\mu_0 = 0.1$	$\mu_0 = 0.25$	$\mu_0 = 0.5$	$\mu_0 = 0.75$	$\mu_0 = 1$
0.5	0.85	0.0291	0.0161	0.0306	0.0441	0.0616	0.0754
1.65	2.85	0.0533	0.0312	0.0636	0.094	0.146	0.190
3	5.10	0.0713	0.0475	0.0995	0.157	0.217	0.307
6	10.2	1.101	0.0644	0.134	0.244	0.330	0.458
10	17.0	0.1302	0.0780	0.166	0.295	0.415	0.627
15	25.5	0.1595	0.089	0.185	0.335	0.514	0.708
20	34.0	0.184	0.090	0.198	0.362	0.545	0.738
35	59.5	0.244	0.092	0.210	0.396	0.586	0.748
50	8.50	0.291	0.095	0.220	0.411	0.609	0.763

The values in the foregoing table show how the fixation of maleic *N*-methylimide²⁸ depends on different factors, in effect:

(1) If curves of M_m as a function of μ_0 for different values of A_m are constructed, a group of practically straight lines are obtained (see Figure 1). This shows that, under the particular conditions used in the experiments, the quantity of maleic *N*-methylimide fixed on the rubber is directly proportional to the quantity added.

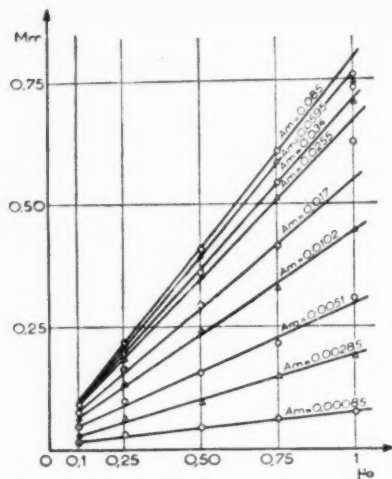


FIG. 1.—Quantity of maleic *N*-methylimide combined with rubber in 16 hours at 130° C (M_m) as a function of the quantity added (μ_0) for different quantities of *p*-bromobenzoyl peroxide (A_m). M_m , μ_0 , and A_m are expressed as gram-molecules per isoprene group.

(2) The curves of M_m as a function of A_m (see Figure 2) show that, above a certain value of A_m , the fixation of maleic *N*-methylimide becomes definitely established. It is then unnecessary, if it is desired to bring about a high fixation of maleic *N*-methylimide, to introduce an amount of *p*-bromobenzoyl peroxide greater than that which might be called the "optimum" amount.

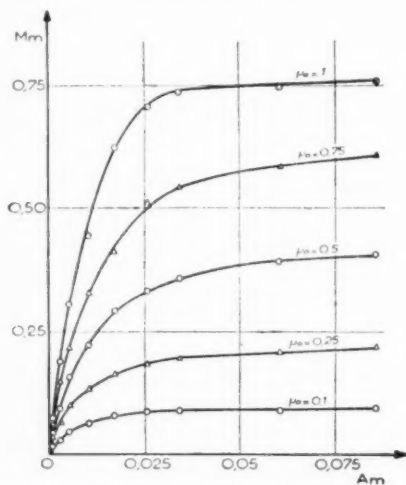


FIG. 2.—Quantity of maleic *N*-methylimide combined with rubber in 16 hours at 130° C (M_m) as a function of the quantity of *p*-bromobenzoyl peroxide added (A_m) for different quantities of maleic *N*-methylimide added (μ_0). M_m , A_m , and μ_0 are expressed in gram-molecules per isoprene group.

If, now, one constructs curves of M_m as a function of $\sqrt{A_m}$ (see Figure 3), it will be seen that the first few points on each of the curves lie on straight lines, and correspond to values which are lower than the optimum amount. It can, therefore, be concluded that the amount of maleic *N*-methylimide which is fixed is, in effect, proportional to the square root of the content of *p*-bromobenzoyl peroxide added, at least for small proportions of the latter.

The results obtained in this series of experiments show, furthermore, (1) that the smaller the proportion of maleic *N*-methylimide added initially, the greater is the proportional fixation of this compound, and (2) that the proportional fixation of brominated free radicals liberated by the decomposition of the peroxide is, in general, of the order of 50 per cent, a fact which seems to

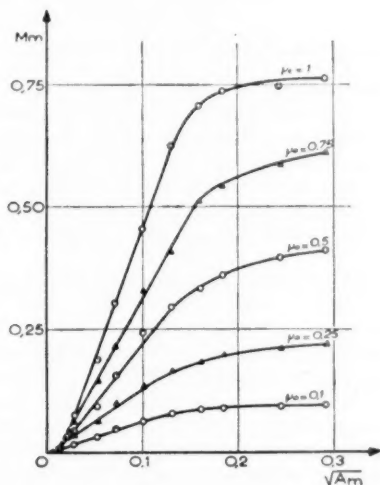


FIG. 3.—Quantity of maleic *N*-methylimide combined with rubber in 16 hours at 130° C (M_m) as a function of the square root of the quantity of *p*-bromobenzoyl peroxide added ($\sqrt{A_m}$) for different quantities of maleic *N*-methylimide added (μ_0). M_m , A_m , and μ_0 are expressed as gram-molecules per isoprene group.

confirm that *p*-bromobenzoyl peroxide breaks up into two free radicals, one of which becomes fixed on the rubber, the other of which forms *p*-bromobenzoic acid, which was identified experimentally.

The next problem was to follow the reaction as a function of time. If M_m (the number of gram-molecules of maleic-*N*-methylimide fixed per isoprene group) is plotted as a function of time for different values of A_m (the corresponding number of gram-molecules of *p*-bromobenzoyl peroxide), it will be found that fixation takes place very rapidly at first, *i.e.*, for 25–35 minutes, and then continues much more slowly (see Figure 4). This corresponds fairly well to the curves of P_m (the number of *p*-BrC₆H₄C(:O)O* groups, calculated on the basis of gram-molecules of *p*-bromobenzoyl peroxide, fixed by one isoprene group) as a function of time (see Figure 5), which show that the brominated free radicals liberated by *p*-bromobenzoyl peroxide and fixed by the rubber are formed by a reaction which is at first very rapid, but which later proceeds at an almost constant rate.



Fig. 4.—Quantity of maleic *N*-methylimide combined with rubber at 130° C (M_m) as a function of time for different quantities of *p*-bromobenzoyl peroxide added (A_m). M_m and A_m are expressed as gram-molecules per isoprene group.

These curves make possible two important conclusions:

(1) As soon as the peroxide is completely decomposed, which is after a rather short time (of the order of 35 minutes), fixation of the brominated free radicals can no longer take place, since their source has disappeared.

(2) Fixation of maleic *N*-methylimide, which takes place at a very rapid rate during the time when the peroxide is decomposing, becomes considerably slower as soon as this decomposition is complete, and then continues, probably by the action of heat alone, but at a much slower rate.

The ratio of the rates of these two reactions is close to the order of 1 to 150–200.

These conclusions were verified experimentally. In fact, by heating a 3 per cent solution of rubber (which had previously been heated in a vacuum to free it of natural peroxides) in benzene at 130° C with the same proportion of maleic *N*-methylimide as before, i.e., 0.5 molecule per isoprene group, but this time without *p*-bromobenzoyl peroxide ($A_m = 0$), a straight line is obtained, as shown in Figure 4, which represents the slow uncatalyzed reaction.

It should be noted that, independent of the fact that combination of rubber with maleic *N*-methylimide by heat alone was considered to be possible on the basis of logical reasons, such combination had already been known to take place with certain other ethylenic compounds, for Farmer²⁹ had combined maleic esters with rubber, without the aid of a catalyst, by heating around 220° C. Also, the Rubber Foundation of Delft, Holland, has recently obtained a patent³⁰, according to which maleic anhydride or acrolein can be made to com-

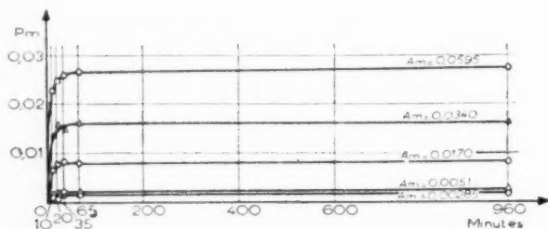


Fig. 5.—Quantity of *p*-BrC₆H₄C(=O)O-groups combined with rubber at 130° C (P_m) as a function of time for different quantities of *p*-bromobenzoyl peroxide added (A_m). P_m and A_m are expressed as gram-molecules per isoprene group.

bine with rubber, in the absence of both a solvent and a catalyst, simply by heating around 150°C .

In view of the rapidity with which the peroxide decomposes at 130°C , it is difficult to make a kinetic study of the reaction at this temperature. It is, however, possible to operate at lower temperatures, for example, at 60°C .

The curves of Figures 6 and 7 show, respectively, the M_m values (number of gram-molecules of maleic *N*-methylimide combined per isoprene group) and the P_m values (number of brominated free radicals fixed by one isoprene group, calculated as molecules of *p*-bromobenzoyl peroxide) as a function of the time, where the initial *p*-bromobenzoyl peroxide is 0.017 molecule per isoprene group.

From Figures 6 and 7 it is obvious that the fixation of maleic *N*-methylimide on the one hand, and of brominated free radicals on the other hand, remains

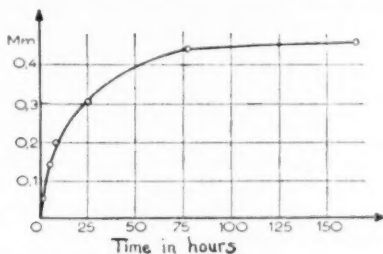


FIG. 6.—Quantity of maleic *N*-methylimide combined with rubber at 60°C (M_m) as a function of the time. M_m is expressed as gram-molecules per isoprene group.

practically constant after 75 hours. If these curves are compared with the curves of Figures 4 and 5, it will be found that the rate of the reaction is approximately 130 times slower at 60°C than it is at 130°C , a fact which should not be regarded as surprising.

Finally, the curve representing the M_m/P_m ratio as a function of time (see Figure 8) is made up essentially of two straight lines which meet at a rather sharp angle at the 8–10 hour range. This indicates that, up to this point of time, the rate of fixation of maleic *N*-methylimide is much greater than the rate of fixation of brominated free radicals, and that, beyond this point, the ratio of the two rates continues practically constant.

This would lead to the conclusion that there is probably a chain reaction which is initiated by the peroxide, is propagated by intervention of the maleic *N*-methylimide alone, and is terminated by fixation of brominated groups.

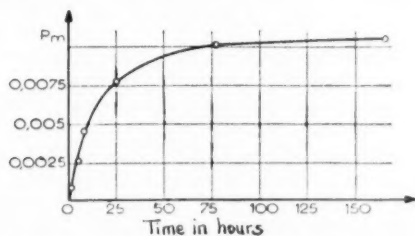


FIG. 7.—Quantity of $p\text{-BrC}_6\text{H}_4\text{C}(:\text{O})\text{O}-$ groups combined with rubber at 60°C (P_m) as a function of time. P_m is expressed as gram-molecules of *p*-bromobenzoyl peroxide per isoprene group.

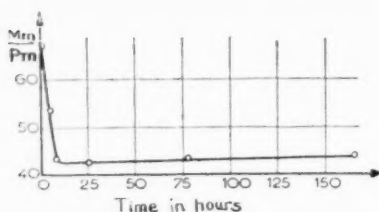
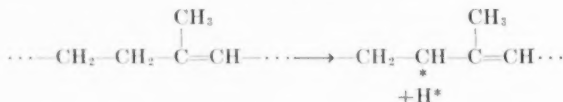


FIG. 8.—Ratio of the quantity of maleic *N*-methylimide combined with rubber at 60° C (M_m) to the quantity of combined *p*-BrC₆H₄C(CO)O-groups (P_m) as a function of time. M_m and P_m are expressed as gram-molecules per isoprene group.

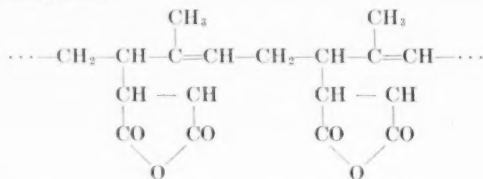
THE STRUCTURE OF ADDITION COMPOUNDS OF RUBBER AND UNSATURATED COMPOUNDS

Bacon and Farmer⁴, and later Le Bras and Compagnon⁹, had at first concluded that the fixation of maleic anhydride is at the double bonds of the rubber molecule. However, almost at the same time, Adler, Pascher, and Schmitz²¹ discovered the substitutive addition of maleic anhydride to simple olefins. Moreover, Farmer²² advanced the hypothesis that the addition of maleic anhydride takes place by a similar process on the chain molecules of rubber. These latter are, in fact, capable of dissociating under certain conditions, with formation of free radicals at the α -methylene atoms:



Farmer believed that, when benzoyl peroxide is the agent employed, this liberation of free radicals is promoted by radicals which are formed from the decomposition of the peroxide.

The radicals of rubber then fix the ethylene compound, the double bond of which thereby disappears:



In this way, the double bonds of rubber remain intact.

Experiments have verified this hypothesis, for numerous determinations of the unsaturation (measured by the iodine value) carried out on products prepared with maleic *N*-methylimide as agent have shown that the major part of the latter unites at points other than at the double bonds of the rubber.

The iodine numbers of products formed by the action of maleic *N*-methylimide in the presence of *p*-bromobenzoyl peroxide were determined, and from the results, curves of the diminishing unsaturation (based on 100 grams of rubber) in relation to the M_m value (number of gram-molecules of maleic *N*-methylimide fixed by 100 grams of rubber) for different values of the initial

quantity, μ_0 , of maleic *N*-methylimide were constructed. All these curves (see Figure 9) were found to lie between the OM_m axis and the straight line OA. This straight line OA represents what would be the variation in saturation S if each molecule of maleic *N*-methylimide which combines had caused the disappearance of one double bond of the rubber.

It can, then, be affirmed that at least part of the maleic *N*-methylimide which becomes fixed is fixed elsewhere than at the double bonds. However, there is a certain decrease of unsaturation, and it can be demonstrated that this

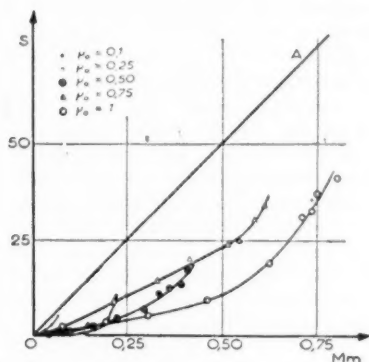


Fig. 9.—Reduction of unsaturation of rubber (S) as a function of combined maleic *N*-methylimide for different quantities of maleic *N*-methylimide originally added (μ_0). M_m and μ_0 are expressed as gram-molecules per isoprene group.

decrease is a result more of the fixation of brominated free radicals liberated from the peroxide than a result of the fixation of maleic *N*-methylimide itself.

Let us turn, for example, to a series of experiments where $\mu_0 = 1$ (μ_0 represents the number of gram-molecules of maleic *N*-methylimide introduced per isoprene group). For the sake of greater clarity, let us construct independently on a graph (see Figure 10) a curve of S as a function of M_m (the continuous curve) and a curve showing P_m (the number of $p\text{-BrC}_6\text{H}_4\text{C}(\text{:O})\text{O}^*$ groups fixed by each isoprene group) as a function of M_m (the broken-line curve). The scale chosen for the P_m values is such that the point corresponding to S

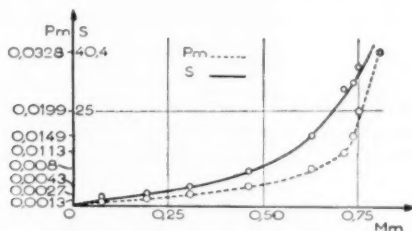


Fig. 10.—Reduction of unsaturation of rubber (S) as a function of the quantity of combined maleic *N*-methylimide (M_m) for a quantity of maleic *N*-methylimide added corresponding to 1 gram-molecule per isoprene group. There is also shown the quantity of $p\text{-BrC}_6\text{H}_4\text{C}(\text{:O})\text{O}^*$ groups combined with rubber (P_m) as a function of the quantity of combined maleic *N*-methylimide (M_m). M_m and P_m are expressed as gram-molecules per isoprene group.

40.4 (for $M_m = 0.763$) is the same as that corresponding to $P_m = 0.0328$ (the value found by a bromine determination). A comparison of these curves shows that their courses are to a certain extent similar, and this shows clearly that the decrease of unsaturation found experimentally depends chiefly on the peroxide and not on the addition of maleic *N*-methylimide.

The process by which these radicals add to the rubber is still unexplained; however, it may be theorized that they unite at the double bonds in accordance with a hypothesis advanced by Farmer to explain the mechanism of vulcanization by benzoyl peroxide³³. It is likewise reasonable to assume that these radicals bring about a scission of the macromolecules at the double bonds and thereby attach themselves to the ends of the fragments formed.

Farmer and his collaborators³⁴ have, in fact, shown that the oxidation of rubber by oxygen results in the formation of hydroperoxidic groups, on the atoms of α -methylenic carbon, and that, as a result, these groups bring about cleavage of the chains at the double bonds. It is probable, therefore, that *p*-bromobenzoyl free radicals behave in a similar manner with the active oxygen which is formed by dissociation of the hydroperoxidic groups.

In spite of certain reservations, therefore, these results confirm from a general viewpoint the views of Farmer. Furthermore, it seems to be established that none of the α -methylenic carbon atoms in rubber can fix more than one molecule of an ethylenic compound, for, in various tests which were carried out, the theoretical value of one molecule of combined maleic *N*-methylimide per isoprene groups was approached, but in no case reached.

MECHANISM OF THE REACTIONS

Although the structure of the addition compounds studied seem to be fairly well established, this is not true of the mechanism of their formation, because the chemical behavior of rubber is of great complexity. Hence one must still be content with hypotheses. Nevertheless, it would seem that a chain reaction in which free radicals take part is involved in the process.

If one designates as A-A the peroxide molecule which is capable of producing two free radicals A*, RH the rubber molecule (H being the mobile hydrogen atom on each isoprene group), and E the molecule of ethylene compound, then the peroxide decomposes according to the following equilibrium reaction:



These A* radicals are capable of bringing about the formation of free radicals on the rubber chains, according to an initiation reaction:



where AH represents the *p*-bromobenzoic acid which actually has been proved experimentally to be formed. The R* radicals then fix themselves to a molecule of the ethylene compound E by a propagation reaction taking place in two steps:



and so forth. REH is, therefore, an addition compound.

There are several possibilities with respect to termination reactions which lead to the formation of intermolecular bonds, thus:



or



or



Finally, the A^* radicals (brominated free radicals when *p*-bromobenzoyl peroxide is used as the reagent) fix themselves on the α -methylenic carbon atoms:



or on the double bonds. This explains in part the decrease in unsaturation which is observed experimentally.

CHARACTER OF THE PRODUCTS

The addition compounds of rubber and maleic *N*-methylimide resemble those which Bacon and Farmer prepared from maleic anhydride. Depending on the proportion of maleic *N*-methylimide, one passes from elastic products similar to rubber to yellowish fibrous products, and then to white amorphous powders having no rubberlike properties. The solubility changes in the same sense, in that the conversion products become increasingly soluble in hot alcohol and in cold acetone.

CONCLUSIONS

It has been shown that, by the simultaneous use of maleic *N*-methylimide and *p*-bromobenzoyl peroxide, it is possible to gain an insight into the fixation of ethylene compounds to rubber in solution. The investigation has made it clear that the presence of a peroxide is not indispensable, since the reaction continues even after the peroxide is completely decomposed, although at a much slower rate. Furthermore, by raising the temperature, it is possible to fix maleic *N*-methylimide in a relatively short time. The results of an experimental study of this thermal reaction in the absence of a catalyst are to be published later.

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GR-S AGING IN SOLUTION *

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It has long been recognized¹ that the viscosity changes in rubber solutions under light depend in a complicated way on oxygen and on the effect of various promoters, retarders, and modifiers on the autoxidation and polymerization reactions involved. Stevens² has shown that a number of substances drawn from both pro- and antioxidant types have the effect of promoting photogelation when used in low concentration and retarding photogelation when used in high concentration. A partial answer to this seeming paradox appears to be in the discoveries connected with redox systems of polymerization. The use of aliphatic amines, for example, to initiate cold polymerization³ gives confirmation of the view⁴ that the induced decomposition of a peroxide gives a free radical as a byproduct. This free radical may be the cause of subsequent

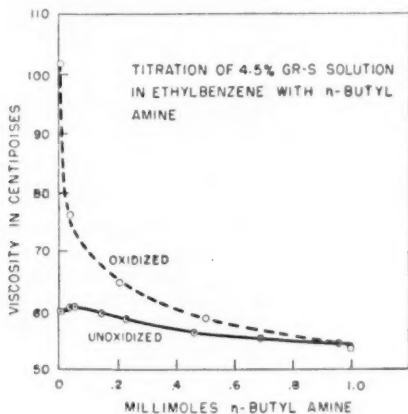


Fig. 1.

polymerization or autoxidation steps before it, too, interacts with the amine and presumably dehydrogenates the amine to form a nitrogen radical. This nitrogen radical attacks the peroxide and a new cycle of the chain reaction ensues.

If an amine, such as *n*-butylamine, is added portionwise to a solution of peroxidic GR-S, there is a nearly instantaneous decrease in viscosity. Equilibrium is reached within a few minutes, and a further decrease results after another portion of amine is added until an end point is reached; after this the

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further addition of amine produces little effect. Figure 1 shows amine titration curves for solutions (in ethylbenzene) of aged and unaged GR-S.

EXPERIMENTAL

A 10 per cent solution of soluble GR-S (X274) in ethylbenzene was prepared and precipitated in ethanol by means of a Waring Blendor. The precipitated GR-S was then redissolved without drying, and the residual alcohol was distilled off under reduced pressure. The operations were conducted under nitrogen containing less than 0.01 per cent oxygen and at room temperature or below. The final concentration of GR-S in ethylbenzene was 4.5 per cent.

The intrinsic viscosity of the GR-S in ethylbenzene was 2.1.

The GR-S solutions were aged by exposure to air at various temperatures in diffuse daylight. The duration of exposure is indicated in the key to Figure 5 and the peroxide content in Table I. During the aging of the GR-S solutions some viscosity increase occurred (Figure 2).

TABLE I
PEROXIDE CONTENT OF AGED GR-S SOLUTIONS OF FIGURE 5

Sample	Peroxide molarity* $\times 10^{-4}$
Unaged	1.3
B	1.9
B	3.8
C	4.6
D	9.4

* Ferrous sulfate analysis.

Viscosity measurements.—Two viscometers were used for the photo-degradation measurements reported here (Figures 3 and 4). The data of Figure 6 were measured on the tilting viscometer shown in Figure 3; those of Figure 7 were obtained with the apparatus shown in Figure 4. An AH-4 lamp was used in both cases. The cell of the tilting viscometer had glass windows 1.5 mm. thick and 1.4 inches in diameter, with 1.6 inches length between windows; the windows were slightly convex. The viscometer was joined at the 0.5-inch neck opening and emptied through a 1.6-mm. capillary, dipping into the cell. An ultraviolet filter (Wratten No. 2) placed in the light beam with the apparatus of Figure 4 showed that degradation proceeded

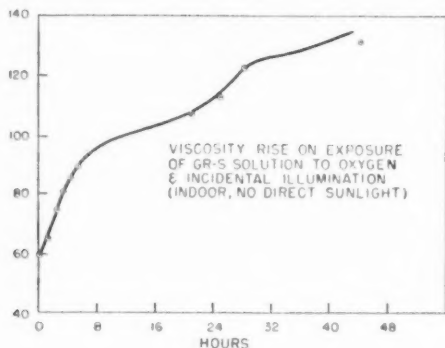


Fig. 2.

fairly rapidly with visible light alone. In neither apparatus was agitation sufficient to give uniform absorption throughout the mass, but at the time of measuring the viscosity the solution was mixed until consistent readings were obtained. (Three consecutive readings did not vary over 0.2 cp.) The light source was placed 2.2 inches from the window of the tilting viscometer, and the temperature just inside the window was 32° C. With this cell there was observed no initial viscosity rise. However, a little gel formation on the

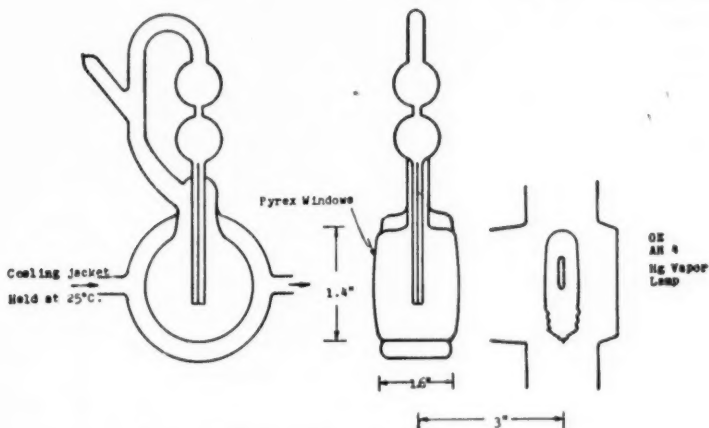


Fig. 3.—Tilting viscometer for photodegradation measurements.

window was observed. In the test of the effect of oxygen on photocission the cell and light were immersed in water to eliminate the possibility of thermally initiated autoxidation. The tests reported in Figure 7 were made in the presence of air.

Viscosity measurements were made by loading the capillary and measuring the fall time. The loading was accomplished by suction in the viscometer of Figure 4 and by tilting in that of Figure 3. The viscometers were calibrated with a solution of known viscosity.

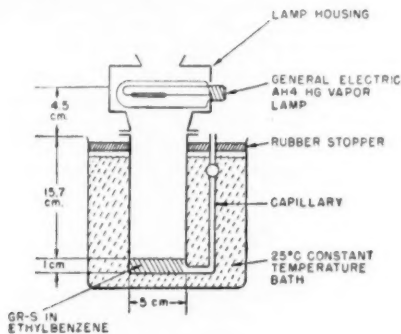


Fig. 4.—Alternate viscometer

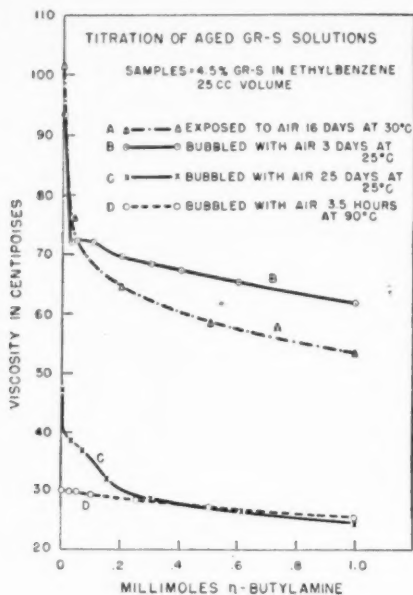


FIG. 5.

Viscosity Rise Anomaly.—Comparison of curve B of Figure 6 and curve A of Figure 7 shows that there is an initial viscosity rise in the one instance but not in the other. This discrepancy was traced to an interesting phenomenon. Curve A of Figure 7 was obtained in the viscometer of Figure 4, and curve B of Figure 6 in the tilting viscometer which was of a cell type and was closed. Some evaporation occurred during measurements in the open viscometer. This amounted to 0.36 per cent per hour and the GR-S concentration rose from 4.5 to 4.9 per cent in a 24-hour period. No correction was made for the effect on viscosity of this change.

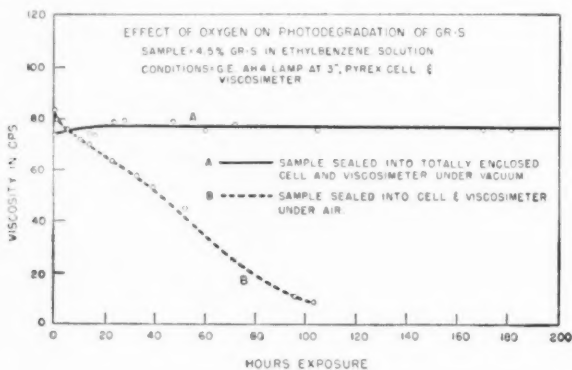


FIG. 6.

The photogelling of natural rubber solutions in carbon tetrachloride has been studied by Buckingham and Planer,⁵ who found that the gel time varied considerably with rubber concentration over the narrow range studied (0.5 to 0.65 per cent). In the GR-S solutions studied by the authors, there was no change in viscosity, in a closed cell containing oxygen, under diffuse daylight for 20 hours at 25° C, and the decrease in viscosity produced by the addition of *n*-butylamine was less than that of the unexposed sample. On sweeping the surface of the solution with air, there was observed a viscosity increase. This was true also when the viscometer was illuminated by ultraviolet light. In this instance when the air stream was replaced by a nitrogen stream the viscosity continued to rise. This seemed to indicate that superficial evaporation favors cross linking.

Formation of peroxide.—Figure 6 shows the viscosity decrease obtained by the addition of amine to several GR-S solutions which had been aged in different ways. With the exception of the solutions already degraded by

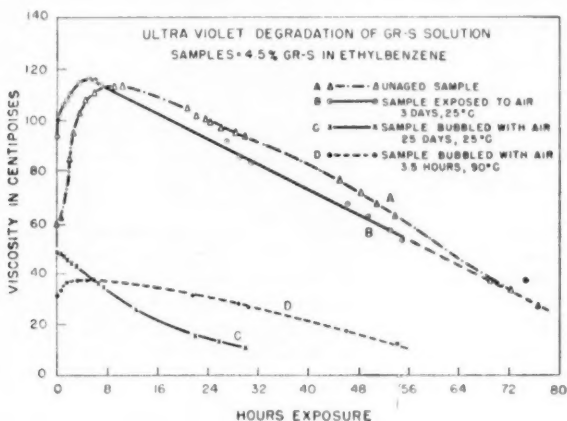


Fig. 7.

severe aging, the viscosity decreased to approximately that of the unaged solution. This may be a coincidence, or it may indicate that photogelling involves the formation of an intermolecular peroxide structure that is susceptible to induced scission.

The viscosity of the GR-S aged at 90° C was relatively unaffected by the addition of amine. Inasmuch as this solution was highly peroxidic (Table I), this fact suggests that two different types of peroxide are formed in GR-S. Previous workers have noted the apparent presence of both a labile and a stable peroxide⁶.

The first indication obtained in this work of the presence of two types of peroxide in GR-S was in oxygen uptake rate measurements made at 90° C in darkness. The rate (Figure 8) was highest at the beginning of exposure, and it seemed that the sample, a GR-S solution aged at room temperature, contained a higher peroxide concentration than the steady state value tolerated at 90° C. However, peroxide analysis showed that at the end of the run the peroxide content was higher than at the start. The possibility of a progressive

development of a retarding impurity was discarded because adding a portion of a degraded sample to a fresh sample did not have a pronounced effect. Moreover, with an unaged sample of GR-S solution the rate continuously rose until a steady rate was obtained. The absence of the initial high rate is no doubt due to the absence of the unstable peroxide.

Oxygen Uptake Measurements.—To determine the rate of oxygen absorption, air was pumped at a constant rate (95 cc. per hour) using a dual syringe pump⁷ through 10 cc. (13 cm.) of GR-S solutions at 90° C. The oxygen concentration of the downstream gas, after passing through a condenser was determined by means of a Beckman (magnetic) oxygen analyzer⁸; the difference in oxygen concentration of the exit gas and air permitted calculation of the rate of oxygen absorption by the rubber. A mole of GR-S was assumed to be 71 grams, which is the weight required to provide a gram-molecular weight of a polymer-

TABLE II
PEROXIDE ANALYSIS OF OXYGEN UPTAKE REACTION MIXTURE (FIGURE 8)

Start End	46 510	Peroxide molarity $\times 10^{-4}$	
		Curve A	Curve B
		1.3	49

ized butadiene unit. This figure is based on the assumption that the soluble GR-S contains 76 per cent butadiene. The standard deviation of the oxygen uptake measurements was 0.13×10^{-2} mole per mole of GR-S per hour.

Peroxide Analysis.—Peroxide analysis (Table II) was made by a titanous chloride procedure. A solution of 0.1 *N* ferrous ammonium sulfate (10 cc.), 1:1 sulfuric acid (2 cc.), and 10 per cent potassium thiocyanate (5 cc.) in methanol (100 cc.) was allowed to stand in the dark for 15 minutes, and was then decolorized with 0.02 *N* titanous chloride. The sample (25 cc.) was added, and the solution shaken and allowed to stand in the dark for 2 hours. It was then titrated with 0.02 *N* titanous chloride. The titanous chloride was standardized with ferric chloride and potassium thiocyanate before each determination.

The introduction into the unaged GR-S of a foreign peroxide shown to be subject to induced decomposition (tetralin hydroperoxide) did not give rise to

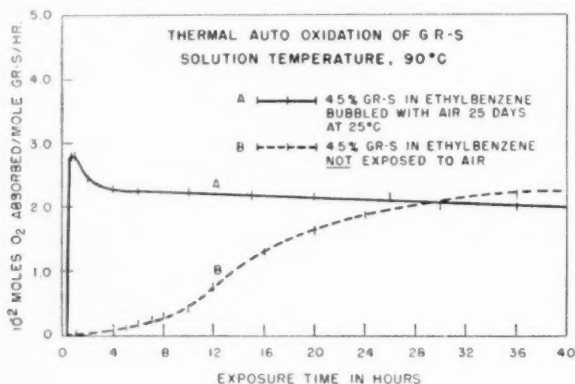


Fig. 8.

pronounced scission on treatment with amine (Figure 9). This shows that the mechanism of induced scission is more specific than an incidental result of catalyzed autoxidation and that probably peroxide links on or between polymer chains undergo induced scission.

Acetic acid also gives rise to induced scission, and it is probable that phenols, aromatic amines, and other types of compounds which promote the decomposition of peroxides will produce induced scission also.

Light stabilization.—It seemed possible that light, like a chemical inducing agent, might seek out the labile peroxide and bring about scission by this mechanism. Figure 6 showed that exposure to oxygen was a necessary condition for the production of an alteration of viscosity under illumination, and Figure 7 showed that the higher the peroxide content of the sample, the earlier scission predominated over the tendency of viscosity to increase. If true, this effect might constitute further evidence that the scission of peroxide linkages is the explanation and not merely the trigger-mechanism of viscosity decrease. The general similarity of the curves of Figure 7 after the initial phase indicates that the effect of light is not very dependent on the type of

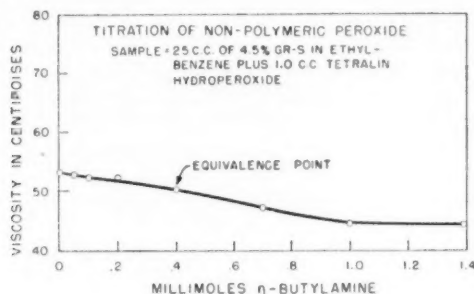


Fig. 9.

peroxide initially present. It was not established whether in these samples the peroxide was the main absorber of the active wave length. (Even visible wave lengths produce a fairly rapid rate of degradation.)

Most light stabilization appears to be achieved by the use of a substance which acts to absorb or reflect the actinic light in a layer near the surface and thus protect the remainder of the mass. It does seem possible, however, that, if it could be found, a compound which is a good antioxidant for GR-S under illumination by ultraviolet light at moderate temperatures would also act as a stabilizer of the viscosity and perhaps of the physical properties in the absence of a solvent.

Amines as stabilizers.—The aliphatic amines, although not of themselves strong ultraviolet absorbers, produced a yellow product when added to the peroxidic GR-S solution. It is, therefore, possible that they produce a photosensitizer effect. This may be the reason why they do not act as light stabilizers in GR-S, although they do so in polystyrene⁹. Table III indicates that the rate of photoscission after the initial phase was not much affected by the presence of the amines. The GR-S solution used for these light stabilizer tests was unaged, but the measurements were carried out in the presence of air. The polyamines produced a rise in viscosity; in fact with polyethylenimine

TABLE III

Amine (0.03 <i>M</i>)	Initial decrease in viscosity, cp.	K^a , photo-scission, %/hour	Steady state O_2 absorption ^b
None (blank) ^c	0	0.12	2.0
<i>n</i> -Butylamine	14	0.11	0.2
Dibutylamine	19	0.10	0.0
Tributylamine	18	0.10	0.0
<i>tert</i> -Butylamine	12	0.12	0.0
Tetraethylenepentamine	20	0.1
Polyethylenimine	..	0.11	0.0
Tetramethyldiaminisopropanol	10	0.18	0.15
Ethylphenylethanamine	7	0.08	0.1

^a First order rate constant.^b Oxygen absorption expressed in 10^{-3} moles O_2 /base mole GR-S/hour after first 15 hours.^c Original viscosity, 51 cp.

some gel particles were observed. The polyethylenimine was dispersed in the ethylbenzene solution by adding the polyethylenimine in alcohol solution.

It was expected that the amines would have some beneficial effect as light stabilizers because they did function as antioxidants at 90° C in darkness. These tests (Table III) were made with an aged 5 per cent GR-S solution in ethylbenzene and 0.01 *M* peroxide concentration in the solution. Subsequently it was observed that the amines were not very effective in controlling oxygen uptake under photoexcitation at 25° (Figure 10). In these results the amount of oxygen absorbed at the time of maximum viscosity was of the general order of magnitude of one per chain.

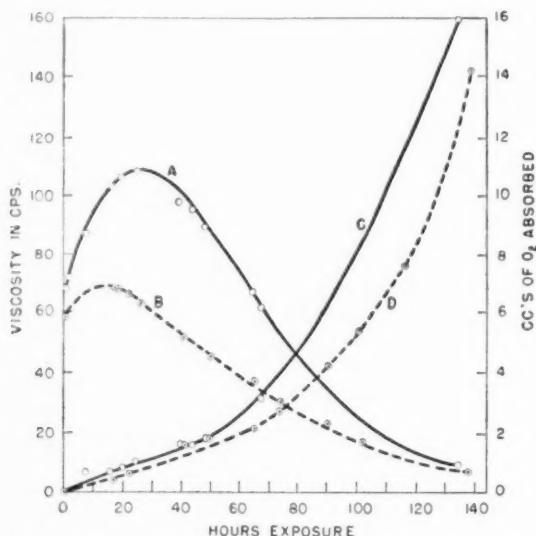


FIG. 10.—Autoxidation of GR-S under ultraviolet light. Sample: 30 cc. of 4.5% solution of GR-S (X-274) in ethylbenzene; Temperature, 25° C; ultraviolet light, AH4 lamp at 3 inches, glass cell; air continuously recirculated through sample at 60 cc. per min. A = Viscosity of sample. B = Viscosity of sample containing *n*-butylamine (0.03 *M*). C = Oxygen absorption of sample. D = Oxygen absorption of sample containing *n*-butylamine (0.03 *M*).

tert-Butylamine.—*tert*-Butylamine was prepared by hydrolyzing 8 grams of *tert*-butyl urea¹⁰ in 75 cc. of diethylene glycol, 10 cc. of water, and an excess of solid sodium hydroxide. This mixture was heated in a steam bath for 3 days; 3.7 grams of *tert*-butylamine was distilled off as it was formed (boiling point, 44° C). A 15-cc. sample was prepared in this way, refluxed over caustic, and redistilled to remove ammonia.

Amine Titration Procedure.—Amine titrations were performed in the viscometer of Figure 4. The amine was added in benzene solution (0.5 *M*) to a 25-cc. sample of GR-S solution.

It was possible to show in a general way that the amine persists in the solution while photoscission proceeds. A solution of unaged GR-S containing 0.3 *M* *n*-butylamine was exposed in the viscometer for 49 hours. The viscosity dropped from 60 to 25 cp. It was then heated at 90° C, and the oxygen absorption rate was less than 10⁻³ moles per hour. An unstabilized sample had a rate of 2.10⁻² moles per mole per hour. There was, incidentally, a residual odor of amine after the light-aging period. There was also sufficient amine left to cause scission in an unexposed but aged GR-S solution on adding some of the exposed solution.

Several hypotheses may be formulated as to why the amines are less effective as antioxidants under photoexcitation than under thermal excitation.

- 1.—The amine oxidation products act as photosensitizers.
- 2.—The temperature coefficient of the initial attack of RO- and ROO-radicals on the antioxidant is considerably greater than that of attack on the GR-S; as a corollary, the steric factor is considerably less.
- 3.—The peroxide formed under photoexcitation undergoes induced decomposition to yield free radicals faster than the amine (in its antioxidant role) can sweep them up.
- 4.—The free radicals generated by photoexcitation are so energy-rich that reaction requires no activation energy; hence it is not selective for the antioxidant.

The second hypothesis is subject to test, for if it were true, the amines would not function as antioxidants at room temperature in darkness. The third hypothesis might be called paint-drier behavior, for such is the probable mechanism of the action of oil-soluble copper cobalt, and iron salts in promoting autoxidation of drying oils. It would have to be assumed in addition that, at high temperatures, either the induced decomposition proceeds less efficiently with respect to free radical generation or that the labile peroxide is not even transiently formed.

CONCLUSIONS

Photoscission of GR-S in ethylbenzene solution has been shown to require the interaction of oxygen. In principle then an antioxidant which is not a photosensitizer should function as a light stabilizer.

The cause of the failure of the antioxidants studied to function as light stabilizers of GR-S is shown to be related to the occurrence of a very low rate of oxidation of the GR-S despite the presence of the antioxidant.

The cause of the viscosity rise in GR-S solutions on autoxidation appears to be the formation of an intermolecular peroxide bond which is subject to induced scission.

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EVALUATION OF THE VULCANIZATION CHARACTERISTICS OF CRUDE RUBBER *

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To define the vulcanization characteristics of crude rubber, planters have recently adopted a plan of technical classification which is based on the modulus at 600 per cent elongation of a standard mixture vulcanized for 40 minutes at 127° C.

Experience acquired during the two years which have elapsed since this plan was put into operation has shown that the choice of this particular test was a fortunate one. The test has, in fact, been found to be simple and rapid enough to make possible the effective control by laboratories of an increasing proportion of the total output of rubber by the plantations of the Far East.

Furthermore, a certain number of manufacturers who have received specification types of rubber in sufficiently large amounts have confirmed the fact that this classification based on the modulus is a good means of distinguishing different grades of rubber.

Nevertheless, because of the very fact that this method is so simple, it does not, as has been proved by a recent study carried out by the French Rubber Institute, always give a good indication of the vulcanization characteristics of crude rubber.

It will be shown that, without unduly complicating the present method of testing the vulcanization characteristics of crude rubber, there is good hope of establishing a criterion which will give a more precise idea of the technical behavior of such rubber¹.

THE SIGNIFICANCE OF THE PRESENT VULCANIZATION

Regarding the formulation of the standard mixture which has been adopted for the specification testing of rubber, it will be found that it gives undercured rubber under the conditions of heating which are specified, i.e., 40 minutes at 127° C.

FORMULATION OF STANDARD MIXTURE

Crude rubber	100
Sulfur	3.5
Mercaptobenzothiazole	0.5
Stearic acid	0.5
Zinc oxide	6

When measurement of the modulus for a time of cure which is much shorter than the time necessary to impart to the vulcanizate its optimum mechanical properties was chosen as a test of the vulcanization characteristics, it was implicitly assumed:

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(1) that any crude rubber can be characterized by a constant which represents the rate of vulcanization of a standard mixture prepared from the particular rubber and, by analogy, of other industrial mixtures of the same type as the standard mixture;

(2) that the value of the modulus of the undercured mixture is an index of the rate of vulcanization;

(3) that the rate of the vulcanization reaction is a criterion by which it is possible to express on a quantitative basis the vulcanization characteristics of rubber mixtures.

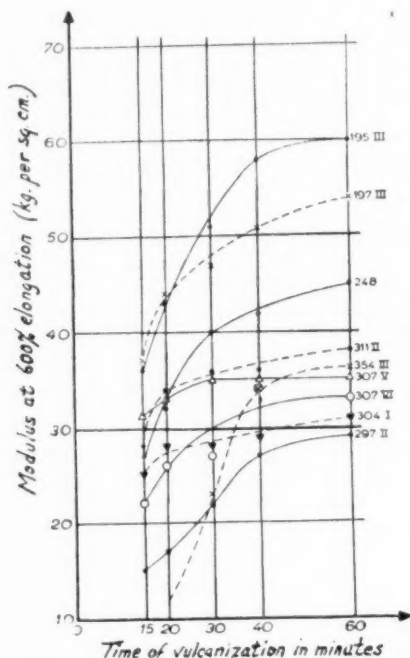


FIG. 1.—Vulcanization curves of nine lots of crude rubber. Standard recipe, with vulcanization at 135° C. Moduli measured on dumbbell test-specimens.

It should be emphasized, before proceeding further, that although a fast rate of vulcanization is unquestionably a property which can be turned to advantage, since it leads to economy of both time and heat expenditure in the vulcanization process, it must not be too great because of the necessity of a margin of safety sufficient for operations preceding vulcanization, such as mixing, extruding, and calendering. The heat effect resulting from these operations may, in effect, start premature vulcanization or scorching if too reactive mixtures are involved.

The question then is, does the rate of vulcanization make it possible to judge on a mathematical basis the vulcanization characteristics of crude rubber simply by classifying from bad to excellent those rubbers which give mixtures

having more and more rapid rates of vulcanization. Actually the best crude rubber for the manufacturer is that which shows itself the most adaptable to every sort of application, and the easiest solution to the problem is most often a compromise between the opposing requirements of rapidity of vulcanization and safety in processing.

Under these conditions, a knowledge of the rate of vulcanization of a crude rubber is valuable because it furnishes information *a priori* on the behavior which is to be feared or expected of rubber mixtures prepared from the particular rubber, but it does not, under actual conditions, lend itself to any final judgment where both the advantage of rapidity of vulcanization and the disadvantage of scorchiness must be taken into account.

Of a much more serious nature are the difficulties which arise when the attempt is made to find out to what extent the measurement of a single modulus value can truthfully characterize the rate of vulcanization of any particular lot of crude rubber.

It is customary to estimate the rate of vulcanization by the course of a complete curve showing the modulus as a function of an extended range of times of vulcanization.

Figure 1 shows vulcanization curves obtained at the French Rubber Institute for vulcanizates prepared from nine different lots of crude rubber, using the standard recipe, but vulcanizing at 135° C, *i.e.*, at a higher temperature than that specified for the standard recipe. These curves have the same general form described by other authors², that is, in each case the modulus approaches progressively a maximum value with increase in the time of vulcanization. The experiments were not carried beyond a time of vulcanization of 60 minutes, for times longer than this would have shown only a decrease of modulus caused by reversion, which is of little significance with this type of mixture.

An examination of the curves in Figure 1 warrant the following general comments:

(1) The vulcanization curves have not, in general, a simple form; in particular, in no part of any of the curves can the modulus be seen to be a linear function of the time of vulcanization.

(2) The vulcanization curves of some of the crude rubbers intersect, and therefore the rate of vulcanization, as defined, for example, by the modulus for a short time of vulcanization, bears almost no relation to the final modulus when the vulcanizate has attained its optimum mechanical properties.

It is quite evident that, under these conditions, the idea of rate of vulcanization is completely misleading from the mathematical view, in that it assumes a linear increase of the modulus as a function of the time of vulcanization. Furthermore, measurement of a single point on the curve, though representative in itself, gives only a very imperfect idea of the rate of vulcanization.

Replacement of the actual curve by an arbitrarily chosen secant or tangent segment has also been considered, but since the number of tests which can be made with any practically acceptable specification is very limited, the most that could be hoped, even in the most favorable cases, would be a very rough approximation. On the contrary, only two different times of vulcanization would be required if the method of testing now to be described were to be adopted.

DEFINITION AND MEASUREMENT OF THE LIMITING MODULUS AND THE VULCANIZATION TIME CONSTANT OF RUBBER MIXTURES

Because of the plateau effect which is characteristic of mixtures of the type of the standard recipe, it is possible in most cases to disregard the phenomenon of reversion and to estimate the decrease in modulus which would result by prolonging the time of vulcanization at 135° C beyond 60 minutes.

If we turn again to Figure 1, we shall see that it is possible to correlate, without introducing any serious error, the actual vulcanization curves with exponential curves in such a way that the modulus tends asymptotically toward a limiting value as the time of vulcanization theoretically approaches infinity.

If it is assumed that the modulus at 600 per cent elongation is a correct index of the degree of vulcanization, then vulcanization must be considered to be equivalent to a chemical reaction of the first order which, for a given rubber mixture, is governed by a definite rate constant. The question here is not whether this hypothesis is scientifically correct, but is merely to ascertain whether it can be made to serve as a basis of a simple specification test for crude rubber.

The simplest type of equation which can be written to represent any vulcanization curve idealized in the foregoing is of the form:

$$M = A(1 - e^{t/E}) \quad (1)$$

In this equation, M represents the modulus at 600 per cent elongation of the standard mixture vulcanized for time t , and A and B are two parameters, adjustment of which makes it possible to bring into coincidence the ideal vulcanization curve represented by an equation of the form of (1) and any actual curve.

It can be easily shown, by extending successively time t toward an infinite value and toward the B value, that the parameter A is none other than the limiting modulus and B is a time constant which indicates the time of vulcanization necessary to obtain any given state of vulcanization.

Before attempting to apply this method to actual cases, for example, to the crude rubbers represented in Figure 1, let us try to decide what sort of agreement may be expected a priori between such a method and actual experimental results.

On the one hand, adjustment of Equation (1) by two parameters alone limits at the same time to two values of the modulus for different times of vulcanization the number of experiments required for the determination of parameters A and B . In principle it should be possible to foresee, with the aid of these parameters, all other possible modulus values for the same rubber mixture. The vulcanization test proposed is, of course, longer than the present specification test, but it is not so laborious that its application should be considered a priori as impractical.

Nevertheless, a greater number of parameters and, consequently, a greater number of states of vulcanization would evidently result in a more rigorous coincidence between the experimental and theoretical curves. With an equation of the form (1), discrepancies in this respect are inevitable, not only for long vulcanization times because of reversion, but also for very short times of vulcanization.

It is known, in fact, that during the initial stage of vulcanization, rubber mixtures remain in the plastic state, and the modulus of the vulcanizate does

not reach a significant value until heating has continued for a certain length of time, which represents its margin of safety from scorching. Equation (1) does not take into account this complication, since it corresponds to vulcanization curves which pass through the zero point of the time of vulcanization.

Basing their work on the theory of Flory and Rehner³, Gee, and Blackwell, Blow, and Fletcher⁴ have shown that it is possible to take into account this lag in the onset of vulcanization by subtracting from the modulus values entering into Equation (1) a constant which can be calculated as a function of the Mooney viscosity of the raw mixture. In the present case it seems that this constant is small enough to warrant its being disregarded in practical work, in the face of the experimental values of the modulus at 600 per cent elongation. Its theoretical calculation would, moreover, involve considerable difficulties, for such high elongations are beyond the limits of validity of the statistical theory of elasticity.

On the contrary, this correction is absolutely necessary in the case of moduli determined at the low elongations used by Gee and by Blackwell, Blow, and Fletcher⁴.

In its foregoing form, Equation (1) does not lend itself well to graphical confirmation, but it can be easily transformed into a linear equation by introducing, in place of the modulus B , a factor C which can be defined as the degree of vulcanization for the time of vulcanization t :

$$C = \frac{M}{A} \quad (2)$$

Equation (1) can then be written:

$$t = B \log \frac{1}{1 - C} \quad (3)$$

Considering any vulcanization curve whatsoever, it is evident that it can or cannot be represented by Equation (1) or (3), depending on whether the points obtained with the factor $\log 1/(1 - C)$ as ordinate and the corresponding time of vulcanization t as abscissa are located or are not located on a straight line passing through the origin of the axes. If the phenomenon of reversion is disregarded, the determination of the limiting modulus A necessary for calculating the degree of vulcanization can be carried out simply by taking the maximum experimental value of the modulus. When this value is not known with certainty, because it would have been necessary to prolong vulcanization too far at the chosen temperature, the limiting modulus can be calculated from the M' and M'' values of the modulus corresponding to two times of vulcanization t' and t'' , where t' is twice the magnitude of t'' .

In this way the following equation is derived from Equation (1):

$$A = \frac{(M')^2}{2M' - M''} \quad (4)$$

In any case where Equation (3) can be accepted as valid, it is possible to deduce from the slope of the straight line representing the vulcanization time constant B :

$$B = \frac{t}{2.302 \log_{10} \left(\frac{1}{1 - C} \right)}$$

At the end of this time of vulcanization, the modulus M of the vulcanizate is a little more than one-half of the limiting modulus A . More precisely, M is then $0.63A$.

APPLICATION OF THE PROPOSED METHOD TO THE MEASUREMENT OF THE STATE OF VULCANIZATION

Table 1 and the curves in Figure 2 give the results obtained in the application of the foregoing method to nine lots of crude rubber, the vulcanization curves of which are shown in Figure 1.

TABLE 1
LIMITING MODULI AND VULCANIZATION TIME CONSTANTS
OF SEVEN DIFFERENT CRUDE RUBBERS
(Vulcanization at 135° C)

Crude rubber	Limiting modulus A (kg. per sq. cm.)	Time constant B (minutes)
195 III	66	19
197 III	55	14
248	47	17
297 II	41	36
307 V	35	7
307 VI	37	19
354 III	53	44

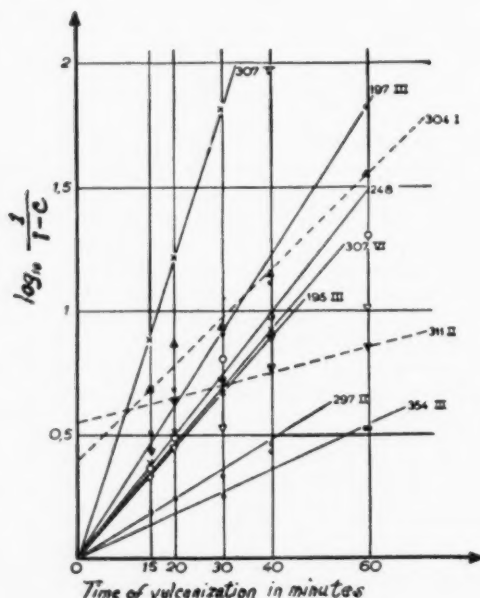


Fig. 2.—The factor $\log_{10} 1/(1 - C)$ as a function of the time of vulcanization for mixtures prepared by the standard recipe from nine different lots of crude rubber.

$C = M/A$, the degree of vulcanization

M = modulus for time t

A = limiting modulus

The values in Table 1 of the limiting modulus A were calculated by means of Equation (4), and it is not therefore surprising that they are definitely higher than the corresponding moduli obtained after vulcanization for 60 minutes.

In spite of a noticeable dispersion of the points representing some of the rubbers, which is to be attributed to experimental errors, these points are located on one or the other side of a straight line passing through the origin for seven of the nine samples of rubber tested.

For rubber samples 304 I and 311 II, however, the straight lines do not pass through the origin. Although the function: $t(\log 1/(1 - C))$ is still linear, there is in these cases no proportionality between this function and the time of vulcanization.

In all the other cases, the measurements of the limiting modulus A and the time constant B would have been possible if only two vulcanizations had been made, for example, 20 and 40 minutes at 135° C.

The number of tests made during the investigation described in this paper is evidently insufficient to pass judgment on the validity of the method. It is

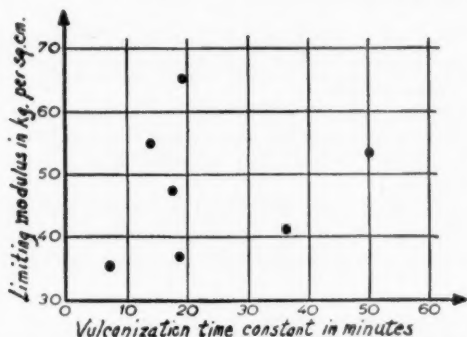


FIG. 3.—Relation between the vulcanization time constant and the limiting modulus.

significant, however, that the method is applicable to the majority of crude rubbers for which it might be used as a technical specification test, but only a statistical study of a very large number of samples would make possible an estimate of its general application.

Nevertheless, it would already appear from the results which have been described that the method can furnish in many cases a logical basis for judging the vulcanizing characteristics of crude rubber by making it possible to distinguish the limiting modulus from the time constant.

Turning again to Table 1, which shows the values of these two properties for the seven samples of rubber which conform to this kind of analysis, it is again evident that the time constant tends to vary within much wider limits than does the limiting modulus itself. Accordingly the method should be an excellent way of distinguishing between different lots of crude rubber from the viewpoint of rate of vulcanization.

Finally it can be seen from Figure 3, which shows the distribution of the points obtained by plotting the limiting modulus as a function of the time constant, that there actually is little correlation between the rate of vulcanization and the absolute values of the modulus.

This shows clearly the necessity of distinguishing between each of these two factors in evaluating the vulcanization characteristics of crude rubber.

CONCLUSIONS

Any vulcanization test of crude rubber which is based on a measurement of the strain modulus for only one time of vulcanization is insufficient as a source of information to the investigator of the rate of vulcanization and at the same time of the order of magnitude of the maximum modulus.

It is proposed to complete this test by a second vulcanization for a different length of time and to correlate the complete vulcanization curves with the exponential functions of time. In this way it seems possible to derive two experimental values of the modulus:

(1) A limiting modulus which characterizes the ultimate stiffness of the vulcanizate.

(2) A vulcanization time constant which serves as an index of the rate of vulcanization of a rubber mixture. The more rapid the rate of vulcanization, the smaller is this constant.

Application of this method to nine different lots of crude rubber proved that by this means it is possible to show well defined differences between various individual lots of crude rubber.

Much more extensive studies will be necessary before it is known whether the method is applicable to the great majority of crude rubbers and whether it is adaptable in its present form to the formulation of a general specification for testing crude rubber.

There is reason to believe that the use of the modulus value at 100 per cent elongation, already proposed by Gee, and his coworkers⁴ instead of 600 per cent elongation, would from this viewpoint offer numerous advantages.

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ABRASION AND WEAR OF RUBBER

ANALYSIS OF WEAR CURVES*

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One of the difficulties of assessing wear test data of rubber articles, *e.g.*, tires, soles and heels, etc., is the fact that the wear index is not necessarily constant throughout the wearing trial. In a previous publication¹ it was suggested that before exact correlations could be established between laboratory and service tests some mathematical method of obtaining constant indexes for both tests must be found. In the subsequent discussion of this paper² at Birmingham, the author revealed that wear curves obtained on the Martindale abrasion tester and also some actual road wear curves could be expressed satisfactorily by an equation of the type $y = ax^n$.

Since that time further work has been done, and it is now proved that if wear curves obtained on a wide range of laboratory machines, *e.g.*, Martindale, du Pont, and Dunlop (Lambourn), are plotted, these curves are all of the same family $y = ax^n$. Although this equation is purely empirical, it is of considerable interest to the rubber industry in that it has such a broad application in the field of laboratory abrasion testing and also in service wear trials.

The importance and usefulness of this method of analysis can probably be illustrated most convincingly by examples from two such widely different fields as that of rubber proofings and road wear tests. Vulcaprene-A was discovered at Blackley during the 1939-45 war, and one of the outlets developed for this material was as an abrasion resistant leathercloth. The Martindale abrasion test was used in the laboratory evaluation of different compounds, and in 1946 it was found that the Martindale wear curves could be expressed by the equation: $y = ax^n$, where y is the time of abrasion, and x is the weight loss, volume loss or thickness decrease, and a and n are constants. By taking a log-log plot of the data, good straight lines are obtained, and the constant n is the slope of this line and the constant a is the intercept on the vertical axis.

The exact physical meaning of these constants is not clear, but this need not be debated at the present time. The important thing to decide is whether this empirical approach can be used to save both testing time and money and also whether analysis in this way can provide more useful information than the conventional methods, now considered to be inadequate.

In the early work with Vulcaprene-A and other proofed fabrics, the usual practice was to measure the weight, volume, or thickness loss after various times or numbers of revolutions. The most resistant compositions were tested for periods up to 20,000 revolutions, until it was discovered that the wear curves could be described by the above equation. Thereafter it was possible to measure the loss after 1000, 2000, and 3000 revolutions.

From a log-log plot of this data, it was possible to calculate the constants a and n for each material and by substituting these values in the equation

* Reprinted from the *India-Rubber Journal*, Vol. 121, No. 5, pages 180 and 182, August 4, 1951.

TABLE 1
MARTINDALE RESULTS

No. of revolutions	Measured weight loss (grams)	Calculated weight loss (grams)
1,000	0.036	0.035
2,000	0.066	0.064
3,000	0.094	0.091
4,000	0.111	0.117
5,000	0.133	0.143
6,000	0.161	0.166
7,000	0.190	0.192
8,000	0.214	0.216
9,000	0.240	0.240
10,000	0.266	0.263

the loss at any subsequent period, e.g., 20,000 revolutions, could be calculated with confidence. Check tests were carried out at the longer periods of abrasion, and the agreement between the measured and the calculated values was in all cases extremely good. The agreement is illustrated by the typical results given in Table 1.

The fact that abrasion losses at the longer periods could be calculated in this way had the immediate result that considerably more tests could be done on a single Martindale machine than hitherto, and this increased the efficiency and utilization of the testing equipment.

The second example illustrating the use of this technique arises from the data obtained in a statistically planned road wear test³. When different compounds are compared in a road test, one of the conventional methods is to express the results in the form of a wear index, *i.e.*, $100 W_B/W_A$, where W_A is either the rate of wear or the wear of the control compound, and W_B the rate of wear or the wear of the experimental compound. The difficulty is that either the wear index or the "tread rating" (tread rating = $1/\text{wear index}$) varies, depending on the period chosen for calculating these constants, and therefore it is not possible to obtain a single estimate of the wear index.

The wear data given in the published paper have been plotted in a log-log plot and the constants a and n derived. Using these constants, the wear after various mileages has been calculated, and the results obtained with different compounds are given in Table 2. Once more it is seen that there is very good agreement between the calculated and the measured values.

TABLE 2
ROAD TEST RESULTS

Mileage	Wear in 1/100 inch							
	Compound A		Compound B		Compound C		Compound D	
	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated
1651	2.7	2.5	3.0	2.8	3.3	3.1	4.0	3.8
3266	4.4	4.8	5.0	5.4	5.7	5.8	6.7	6.9
4864	6.9	6.9	7.4	7.9	8.1	8.4	9.8	9.8
5896	8.6	8.4	10.0	9.5	10.5	10.1	12.0	11.6
6698	9.6	9.4	10.9	10.8	11.7	11.4	13.2	13.1
7527	10.9	10.5	12.3	12.1	12.8	12.7	14.5	14.5
8327	11.9	11.6	13.5	13.3	14.2	14.0	16.1	15.8
Value of n	0.95		0.97		0.94		0.89	
Value of a	0.0022		0.0021		0.0029		0.0051	

Another point of interest is that the value of n derived from the road wear curves is less than 1. Work with various laboratory abrasion tests has shown that the value of n for a wide range of compounds is usually greater than 1. This is an important point. When n is less than 1 it means that the rate of wear is decreasing as the test progresses, whereas when n is greater than 1 it means that the rate of wear is increasing as the test progresses.

There is little doubt that this significant difference in the wear curves obtained on laboratory machines compared with service has an important bearing on the degree of correlation between the two types of test. It appears, therefore, that most laboratory machines operate under conditions which are too severe for good correlation with service to be obtained with a wide range of compounds.

In other words, the aim of producing an accelerated abrasion test on which results can be obtained quickly has been achieved at the sacrifice of good correlation with service⁴.

The purpose of the present publication is to draw attention to the general application of an equation of the power law type in wear tests, in the hope that those members of industry concerned with wear testing will try the technique on the data available to them.

Only by this means can the true value of the method be assessed from the point of view of road tests, sole and heel wearing trials, and other applications where the wearing qualities of the product are one of the main criteria of its useful life. The author feels that the method merits fuller investigation on this scale, as important savings in time and effort in wear tests could result if the results were analyzed in this way.

Service tests, by their nature, are expensive and if road tests, for example, could be limited to 5000 miles and yet the mileage to wear a given thickness of tread be calculated with the precision necessary to distinguish accurately between compounds, the technique of analysis given here would be justified and not a little progress in wear testing achieved.

Finally, it may also be of interest to record that rate of wear curves can also be described by an equation of the power law type ($y = ax^n$), and in certain applications the rate of wear curves are more useful than wear curves. Wear Indexes calculated from rate of wear curves in the way described are thought to be a truer estimate of abrasion resistance of materials. This subject will be dealt with more fully in another publication.

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BELT-FLEXING TEST OF THE DU PONT TYPE *

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INTRODUCTION

When rubbers are subjected to repeated stressing, small cracks appear on the surface and these grow larger and deeper as the time of stressing is prolonged until the article fails. The conditions which promote the development of cracks in service are still in some doubt, but there is some evidence that oxidation or ozone attack and mechanical fatigue play their part. Because of the complexity of the conditions prevailing in service, probably the assessment of flex-cracking is best obtained from a service test. Unfortunately service tests tend to be expensive and usually cannot be controlled so accurately as is necessary to obtain reliable comparative data on different rubber compounds. It is desirable, therefore, to have laboratory tests which will allow assessment of the susceptibility of a rubber compound to flex-cracking. The laboratory test should possess two features, *viz.*, (1) the results should be sufficiently accurate to discriminate readily between compounds when the difference is of technical importance, and (2) there should be good correlation between the results of the laboratory test and the behavior of the compounds in service. Because of the diversity of conditions met in service, *e.g.*, type and degree of straining, amplitude of dynamic strains, temperature, exposure to light, etc., it would be surprising if any laboratory test satisfied the second requirement for all types of service. Until the mechanism of flex-cracking is better understood, the most satisfactory procedure is to control as accurately as possible the test conditions which appear most important. A study of the effects of the various factors will assist in improving the reproducibility of the test by better control of the test conditions and should at the same time help in elucidating the mechanism responsible for flex-cracking.

Numerous laboratory tests have been devised, but only two are in widespread use and have been recommended in both British¹ and United States specifications², namely, the De Mattia flex-tester and the du Pont belt-flexing machine. Newton³ and Newton and Scott⁴ have studied the De Mattia flexing test in some detail, but the du Pont belt flexing test has not received such detailed treatment.

In this paper, the authors, discuss a test of the du Pont belt-flexing type from the point of view of the testing errors involved, the methods of improving the method of test, and interpretations of results.

MODIFICATION OF THE DU PONT BELT-FLEXING MACHINE

The du Pont belt-flexing machine was described by Neal and Northam⁵, and is also found in the A.S.T.M. Specification D430-40 and in B.S. 903-1950. The machine used for the work described in this paper had been modified by incorporating bent balance arms as specified in B.S. 903-1950 and described

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 27, No. 4, pages 209-222, August 1951.

in detail by one of us⁶. By this means, the belt tension becomes independent of the angle of the balance arm, whereas with straight balance arms the tension tends to decrease as the belt stretches during the test.

This does not mean, however, that variations in belt length can be ignored. With a nominal belt length of 90 inches, the rate of flexure is approximately 400 per minute, but this varies inversely with the length of the belt and tends to decrease during a test as the belt stretches. If it is required that the rate of flexing be controlled within a tolerance of ± 1 per cent, then the balance arm must be kept within an angle of $\pm 6^\circ$. This can conveniently be checked by means of a scale permanently fitted behind the balance arm, the length of the belt being adjusted at intervals by incorporating "blanks" of suitable length. A tolerance of $\pm 6^\circ$ in the angle of the balance arm would cause a variation of about ± 3 per cent in tension if the balance arm is straight. Although the bent balance arm does not completely eliminate the necessity for adjusting the length of the belt, it does control the conditions more accurately throughout a test.

SOURCES OF ERROR

It is general experience that the results of laboratory flexing tests are extremely variable. This is a serious drawback to any test and means that it is impossible to detect relatively small differences between the properties of two compounds. A study of the test errors often helps to reduce them by suitable modification of the test method. In general, the variability can be attributed to variations in the preparation of the test sample, variations of the conditions pertaining to the actual test and lack of precision in estimating the result. Newton and Scott⁴ showed that, when molded test-pieces were used for the De Mattia test, probably the most important source of variation was that arising between nominally identical samples. A statistical study of test errors has been used in this paper to determine the relative importance of a number of factors in the belt-flexing test. It should be noted that where any factor is stated to be statistically insignificant, it may well become significant if the test were improved in accuracy so that smaller effects could be demonstrated. It has been possible to show that certain factors are significant, and these should be looked upon as the most important factors. The analysis of variance⁷ has been used as the statistical technique throughout.

EXPERIMENTAL METHOD

The work described was all carried out on the following compound:

Smoked sheet rubber	100
Zinc oxide	5
MPC Black (Kosmobile-HM)	47.5
Sulfur	3
Vulcafor-MBT	0.85
Stearic acid	3
Vulcaflex-A	1

Cure: 60 minutes at 141° C

The test-pieces were cut with a guillotine from slabs molded in steel molds in a press. Six test-pieces could be obtained from each molded slab.

Four stages of cracking were identified, which are called, for convenience:

pinholes	medium cracks
small cracks	deep cracks

The time (of flexing) for each test-piece to reach each stage of cracking was noted, the belts being examined at frequent intervals, usually every four or every eight hours.

COMPARISON OF SPECIMENS AND LINKAGES

The shape of the test-piece described in both the A.S.T.M. and B.S. Specifications⁸ is shown in Figure 1, and it is recommended that fasteners of the Mastabar type with rawhide pins be used. These fasteners have the disadvantage of weakening the test-piece which frequently tears if the test becomes prolonged. An alternative method is the use of metal chain fasteners which fasten into holes molded in the test-piece and reinforced with fabric

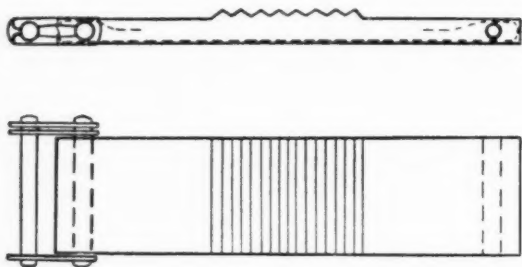


FIG. 1.

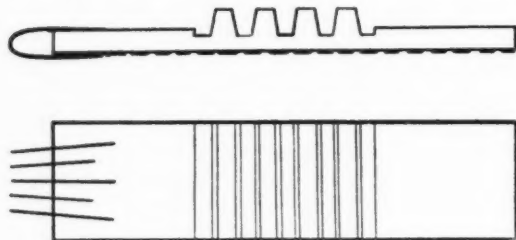


FIG. 2.

inserts (see Figure 1). An alternative test-piece which was in use at Blackley for many years is shown in Figure 2, which also illustrates the Mastabar fastener, showing that the tensile force on the test-piece is concentrated at a few points, whereas it is uniformly distributed by the chain fastener. A change in any feature of the test may have two results, *viz.*, it may alter the rate of flexing and it may affect the variability of the results. Anything which reduces the variability is preferable, and, similarly, shortening of the test within limits is an advantage.

A comparison was made of three belts constructed as follows:

- Belt 1. Specimen A, chain fasteners
- Belt 2. Specimen A, Mastabar clips
- Belt 3. Specimen B, Mastabar clips

Each belt contained twenty-four test-pieces, prepared from four molded slabs of rubber. The belts were run simultaneously on the machine, which had provision for three belts. The position of each belt remained unchanged throughout the test. It will be shown later that the position of the belt on the machine does not have a significant effect, so a comparison of the three belts does provide a comparison of the types of specimen and belt linkage.

The rate of cracking of each type of belt is illustrated in Table 1, which gives the mean flexing time (in hours) to each stage of cracking for each belt.

TABLE 1

Belt	1	2	3
Pinholes	—	37	48
Small cracks	23	56	86
Medium cracks	33	81	112
Deep cracks	41	91	133

Cracking occurs faster with specimen A (standard type) than with specimen B, and (at least with specimen A) the test is appreciably faster if chain fasteners are used instead of Mastabar clips. The latter effect may be explained in terms of the tearing of the test-piece which occurs with the clips and allows the test-piece to relax to some extent.

The variability of the test results was analyzed to determine the variability within a molded slab (that is, between test-pieces cut from one molded slab), which is the test error, since the replicate test-pieces used in the routine test are prepared in this way. It was also possible to assess the significance of the variability between the mean results for the four slabs used to make each belt. Table 2 summarizes the results of the analysis.

TABLE 2

Degree of cracking	Source of variation	Degrees of freedom	Standard deviation			Coefficient of variation (%)		
			Belt			Belt		
			1	2	3	1	2	3
Pinholes	Molded slabs	3	—	†	†			
	Test error	20	—	13.9	17	—	37.6	35.6
Small cracks	Molded slabs	3	**	†	**			
	Test error	20	2.6	12.2	22.1	11.5	21.8	27.3
Medium cracks	Molded slabs	3	†	†	**			
	Test error	20	2.23	16.5	20.7	6.8	20.3	18.5
Deep cracks	Molded slabs	3	†	†	*			
	Test error	20	3.3	15.8	29.1	8.0	16.0	21.9

* Significant at 0.05 significance level.

† Not significant.

** Significant at 0.01 significance level.

Since Table 1 shows a marked difference between the mean rates of flex cracking of the three belts, the coefficient of variation, rather than the standard deviation, should be used as the test error if comparisons of the errors are to be made. It is evident from Table 2 that, even though the rate of flex-cracking is much greater with belt 1, it also has lowest test error. The errors with belts 2 and 3 are similar. The greatest improvement in the test error has, therefore, resulted from the use of chain fasteners instead of Mastabar clips.

It should also be noted that, although the test error is so much larger with belt 3, it has still been possible to detect significant differences between molded

slabs. It seems, therefore, that the replicate molded slabs of type A are more reproducible in flex-cracking properties than those of type B. The lack of reproducibility may result from the considerable flow which takes place during cure and which is necessary to form the deep ridges in the type B specimen. This flow may release strains in certain parts and also introduce strains at other parts, thereby increasing the internal strain heterogeneity of the test pieces.

VARIABILITY BETWEEN MOLDED SLABS

It was shown above that significant differences could be detected between replicate slabs molded from a single compounded stock. A more thorough investigation of this effect is described below, but the experiment was carried out in such a way that a number of additional factors could be examined at the same time. The results could be analyzed to determine the relative effects of:

- (1) replicate test runs.
- (2) belt position on the machine.
- (3) the interaction between the test run and the belt position.
- (4) differences between test slabs.
- (5) test error within test slabs, *i.e.*, between replicate test-pieces from a test slab.
- (6) the test error within duplicate test-pieces tested simultaneously in the same belt.

The experiment was designed as follows. Twenty-seven slabs of the type A specimen were cured from a single batch of the compound quoted earlier, and divided into three sets of nine slabs. Since six test-pieces could be prepared from each slab, the nine slabs provided fifty-four test-pieces, which were made up into three belts using Mastabar fasteners. The six test-pieces from each slab were divided into three pairs, one pair being tested in each belt. The three belts were tested simultaneously. Two further sets of three belts were prepared in a similar manner from the remaining test slabs and were tested in two successive runs.

The complete analysis of variance of the results is given in Table 3.

TABLE 3

Source of variance	Degrees of freedom	Pinholes	Mean square and significance		
			Small cracks	Medium cracks	Deep cracks
Between runs (R)	2	237*	1055***	1028*	1818*
Between belt positions (P)	2	32	54	188	308
R \times P interaction	4	12	12	22	77
Between molded slabs (within runs) (S)	24	56***	146***	210***	336***
S \times P interaction (eliminating runs)	48	14*	15†	30***	48***
Error within duplicate test-pieces	81	8.4	12.4	9.6	13.7

* Significant at the 0.05 significance level.

† Not significant at the 0.05 significance level.

*** Significant at the 0.001 significance level.

Three of the factors were found to be significant, *viz.*:

- (1) S \times P interaction.
- (2) Differences between test slabs.
- (3) Replicate test runs.

$S \times P$ INTERACTION

If the variability between molded slabs is similar, irrespective of the position of the belt on the test machine, there would not be a significant $S \times P$ interaction (where S denotes molded slabs and P denotes position of the belt). As this is not the case, the $S \times P$ interaction should be used as the test error when examining the significance of other factors operating within a test run.

BETWEEN MOLDED SLABS (WITHIN RUN)

There is, beyond doubt, a significant difference between the flexing characteristics of test-pieces cut from different molded slabs, even when tested at the same time. This may be illustrated by the mean results for replicate test-pieces tested in different belts in one run only. In Table 4 where the results have been arranged in a suitable order to show the effect clearly.

TABLE 4

Test slab	Mean time to medium cracks
1	15
2	16
3	17
4	18
5	18
6	22
7	26
8	29
9	29½

Newton and Scott⁴ noted similar differences between molded De Mattia test-pieces and suggested that such an effect might be due to differences in the method of filling the mold or to strains of a varying character arising during molding. It is evident that when such differences can arise with one compound only, it will be a major source of error when successive molding operations involving different compounds are compared.

REPLICATE TEST RUNS

The significance of this factor has been estimated using the variance between replicate molded slabs (within runs) as the test error, since that is the most important source of error within runs. There is a significant difference between test runs at all stages of cracking, and Table 5 shows that the rate of cracking is rather slow in Run 1.

It can be shown by eliminating Run 1 that it alone is responsible for the significance. Since the molded slabs were allotted at random to the particular test runs, it is very unlikely that the run effect can be attributed to marked initial differences between the sets of slabs, and aging of the slabs is also unlikely to be responsible. It would appear, therefore, that the source of this error lies within the conditions of test. It might be a result of a change in the

TABLE 5

Degree of cracking	Run 1	Run 2	Run 3
Pinholes	10½	8½	6½
Small cracks	22½	15	14½
Medium cracks	28	21	21
Deep cracks	32½	27½	26½

conditions of flexing, *e.g.*, speed of running, ambient temperature, or to a change in the assessment of the grade of cracking (although the whole experiment was carried out by one operator). It is significant that such marked changes in the ratio of cracking between runs can occur, but the variability between test-pieces tested in any single run is much lower. This means that useful results can still be obtained from comparative tests carried out as a single experiment.

TEST ERROR

Using the coefficient of variation as a measure of the test error and also basing the estimate of the error on the variability between six replicate test-pieces cut from a single slab (the usual procedure in practice), the average levels of the errors are:

	C. of V. (%)
Pinholes	35-40
Small cracks	20-25
Medium cracks	20-25
Deep cracks	15-20

The errors are very large, particularly at the pinhole stage, and also the test tends to become progressively more precise as it proceeds. It is important to realize, however, that the increase in precision does not necessarily mean an increase in discriminating power, a factor which has not been investigated.

It can be shown that for significance at the 0.05 significance level, the percentage difference between the mean results of two sets of six replicate test-pieces must be greater than $1.28 \times \text{C. of V. } (\%)$. In practice the true error of test is even larger than that indicated above, since it is necessary to allow for the variation between nominally identical molded slabs.

GRADED PHOTOGRAPHS; COMPARISON OF OPERATORS

At least a portion of the test error may be attributed to lack of precision in identifying the various stages of cracking, and it is reasonable to suppose that there will be even greater differences between the results obtained by two operators. One method recommended to reduce both sources of error is the comparison of the test-pieces against standard graded photographs. The value of such a technique was examined as follows. Eighteen test-pieces (Type A) were joined to form a belt which was examined at four hourly intervals by two operators, acting independently. Each operator first graded the test-pieces without assistance and then repeated the assessment using a set of four graded photographs (Figure 3) which had previously been agreed upon by both operators.

The first point to note was that with each operator, quite independently, the use of the graded photographs did not influence the results reported, but the two operators did not necessarily agree in their reports. An analysis of the results is given in Table 6.

In this case the interaction provides a measure of the error which arises from random variations in the assessment of the same test-pieces by the two operators. Expressed as a coefficient of variation the interactions become:

	Interaction	Mean
Pinholes	66 per cent	24.1
Small cracks	44 per cent	52
Medium cracks	16 per cent	88
Deep cracks	9 per cent	104

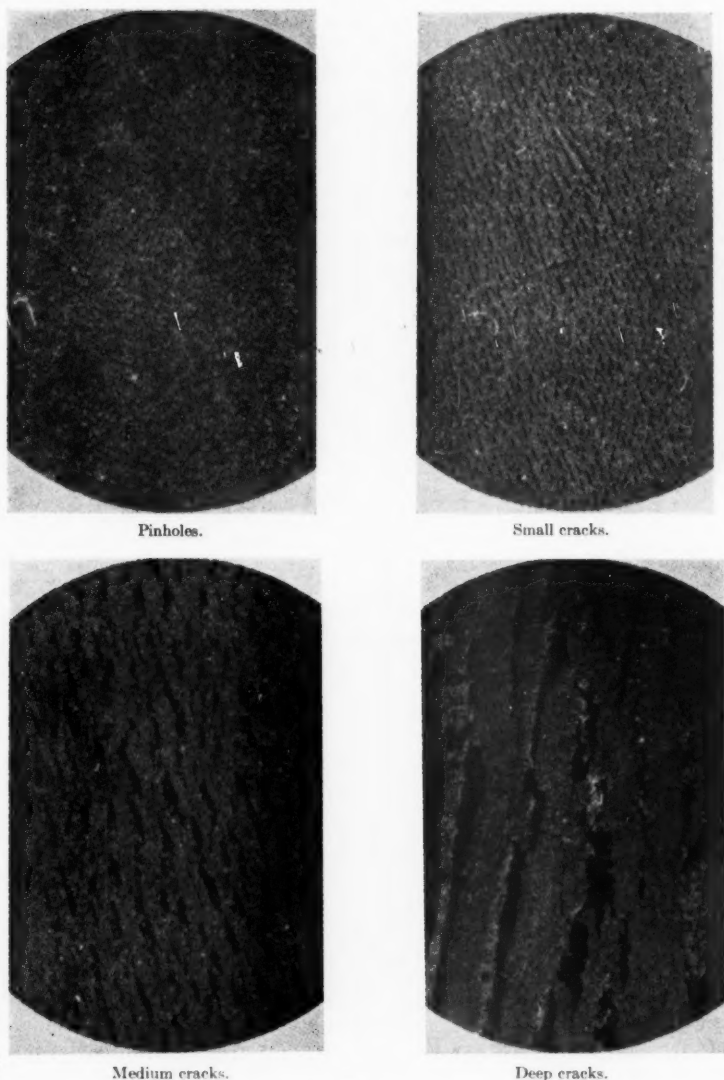


FIG. 3.

and are seen to decrease rapidly as the test proceeds, as was shown earlier for the test errors. It seems possible, then, that some of the test error can be attributed to such random variations in assessment.

The difference between test-pieces was not significant at the pinhole stage, but became increasingly significant as the test proceeded, which confirms that test-pieces exhibit real differences in flex-cracking properties. These differ-

ences cannot be attributed to errors of assessment, as the results obtained by the two operators have been averaged, and it is extremely unlikely that the individual errors of assessment would be additive at each of the four stages of cracking.

The two operators differed significantly in their assessment of the cracking at the intermediate stages of breakdown, but the agreement at the pinhole and deep crack stages was remarkably good. This is undoubtedly due to the fact that the pinhole and deep crack stages are more definite stages to observe in the sense that it is the first appearance of pinholes which is noted. As the cracking proceeds from pinholes to small cracks and from small cracks to medium cracks, both the number and the distribution of the cracks vary from test-piece to test-piece. No two test-pieces crack in such a way as to reproduce

TABLE 6

	Degrees of freedom	Sum of squares	Mean square and significance
Pinholes			
Between operators	1	0.2	0.2†
Between test-pieces	9	1921.8	213.5†
Interaction	9	2829.8	314.4
Total	19	4751.8	
Small Cracks			
Between operators	1	3287	3287*
Between test-pieces	17	20,174	1186.7*
Interaction	17	8845	520.3
Total	35	32,206	
Medium cracks			
Between operators	1	4519	4519 ***
Between test-pieces	16	48,886	3055.4***
Interaction	16	3017	194.8
Total	33	56,422	
Deep cracks			
Between operators	1	2	2 †
Between test-pieces	16	86,869	5404 ***
Interaction	16	1376	86
Total	33	88,247	

in detail the cracking of graded test-pieces or photographs. For example, at the small crack stage the assessment is complicated by the presence of pinholes, and at the medium crack stage there are also pinholes and small cracks present. It is not surprising, therefore, that operators differ in the choice of the particular combination of cracks which are judged to be either the small crack stage or medium crack stage of cracking. By the time the deep crack stage is reached, the majority of the cracks have grown to roughly the same size, and this factor aids the operator when assessing this stage of cracking.

As noted above, comparison of the test-pieces with graded photographs did not influence the results and did not affect the differences between operators. It appears that the operator develops a firm mental picture of the appearance of the test-pieces at each stage of cracking. Different operators apparently

have different mental pictures which are not necessarily adjusted to correspond by using the same graded photographs.

The present authors are of the opinion that graded photographs may be of more use with the De Mattia type of test-piece than with the du Pont. For example, the cracks which occur in the De Mattia test-piece are free to form over the whole area of the central groove. With the du Pont test-piece, cracking is confined by the geometry of the test-piece to a fairly narrow line. There is a fundamental difference in the resulting type of cracking obtained in the two cases. In the case of the De Mattia test-piece there is a tendency for a large number of surface cracks to develop before cracking proceeds in depth into the body of the rubber. The du Pont test-piece, on the other hand, is such that a smaller number of cracks are formed, and these cracks grow into the body of the rubber much earlier than is the case with the De Mattia test-piece. It is well known that the assessment of degree of cracking when the depth of crack has to be taken into account is a problem which still requires solution.

This experiment casts some doubt on the value which can be placed on the use of graded photographs to improve the reproducibility of the du Pont test.

THE TREATMENT OF FLEX-CRACKING RESULTS

The object of a flex-cracking test is to determine the rate at which cracks appear and develop when the rubber test-piece is subjected to repeated flexing. Ideally, it should be possible to quote the result of a test on one material as a single figure indicating the rate of flexing, so that comparisons of different materials may be readily made. It is then necessary for the flex-cracking to proceed at a constant rate or for the data to be in such a form that a constant which is a measure of rate of flex-cracking can be found. In any case, two quantities must be measured, one being the period of flexing or number of flexures and the other can be called the *degree of flex-cracking*. There is no simple quantitative method of measuring the degree of cracking, and it has been customary to define certain specific stages of breakdown, which are illustrated by means of standard samples. The choice of the standard samples is based on a purely visual, subjective, assessment of the appearance (condition) of the sample, relative to the other standard samples chosen. It is found that a number of observers can usually agree as to whether a particular sample represents a stage of cracking which is midway between two other (arbitrary) stages. In other words, if a particular sample is chosen to be representative of any arbitrary stage of breakdown, then by trial one can construct a series of samples covering a range of cracking, and the samples will be equally and regularly spaced as judged by visual assessment. Newton³ claims that if the above conditions are achieved, then the number of flexures to produce each successive grade of cracking increases in an exponential fashion. If the grades are numbered consecutively, there is a linear relationship between the grade number and the logarithm of the number of flexures. It is possible in this case to estimate, from the number of flexures to reach a certain stage of cracking, the number of flexures which would produce another arbitrarily chosen standard grade of cracking, a number of these estimates being obtained in one experiment. For accuracy it is necessary to identify a number of early stages of cracking but, as shown earlier, the results tend to be very variable in the early stages with a test of the du Pont belt type. Further, it has been found that when only four stages of cracking are identified as described in

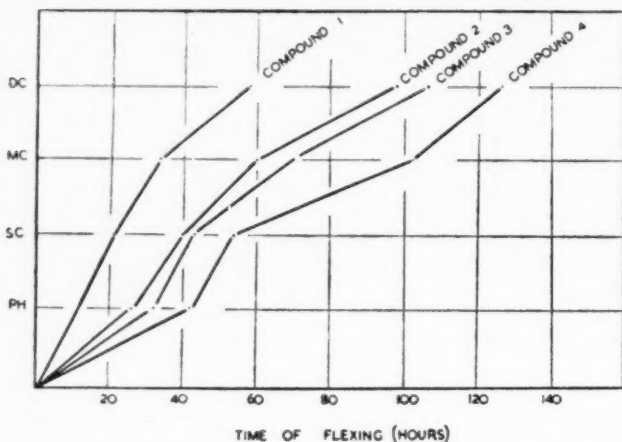


FIG. 4.

earlier sections of this paper, the relationship between the grade of cracking and the logarithm of the number of flexures is seldom linear. Equally, there is seldom a linear relationship between the actual number of flexures and the grade of cracking. For these reasons application of the Newton method is not always satisfactory.

Figure 4 shows the relationship between the grade of cracking and the period of flexing for four compounds tested simultaneously. The results plotted are the arithmetic mean of the results on six test-pieces from each compound. The time scale is linear, and the stages of cracking are assumed to be equally spaced. In no instance is the relationship linear. Considering Compound 4 only, the gradient of the line is seen to change in a somewhat random manner from one stage of cracking to another. Comparison of the four graphs of

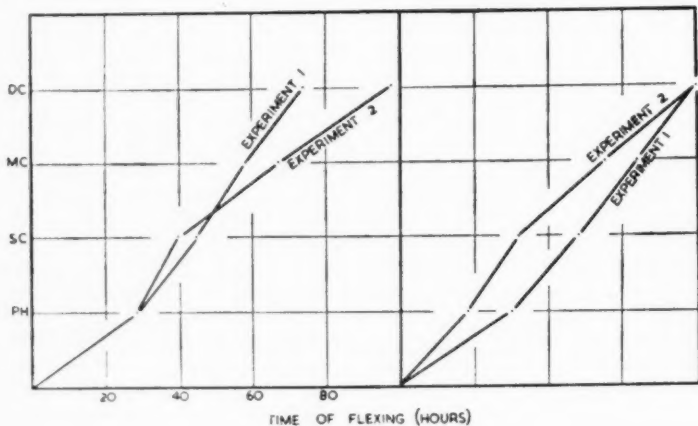


FIG. 5.

Figure 4 shows that there is a trend for the slopes of the lines to change in a similar manner on proceeding from one stage to the next. In other words, there are systematic factors which determine the relative disposition of the grades of cracking quite apart from random effects due to experimental error. The effects of such factors on the results of two entirely separate experiments is illustrated in Figure 5. The grand means of the results of all compounds tested at each stage of cracking was calculated for two separate experiments, called (1) and (2) in Figure 5. In Part A the actual periods of flexing are plotted, but in Part B the time scales for the two experiments are adjusted so that the final points on the curves coincide. The relative disposition of the intermediate stages can be seen. In comparison with Experiment 2, Experiment 1 shows slower cracking at first but faster in the later stages. Thus, in spite of the standardizing of the stages of cracking, their relative disposition

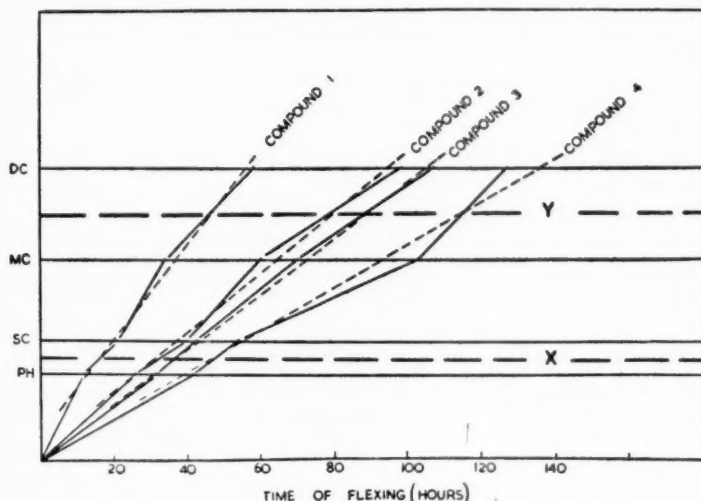


FIG. 6.

(measured in terms of flexing time) varies from one experiment to another. In this case, it would be permissible to modify the relative disposition of the grades of cracking in one experiment and the simplest modification is one which tends to give a linear relationship. The disposition of the stages will, however, vary from one experiment to another.

One method of treating the results obtained in a single experiment is illustrated below.

Consider the set of results plotted in Figure 4 and the corresponding *grand mean* results plotted as Experiment 2 in Figure 5a. The grand mean results are:

Pinholes	28 hours
Small cracks	39.5 hours
Medium cracks	67 hours
Deep cracks	97.5 hours

If the ordinate scale is now modified so that the stages of cracking are distributed in proportion to the grand mean results and the data for each of

the compounds is plotted on this new scale, then Figure 4 becomes Figure 6. Comparison of the two figures shows that the graphs have become definitely straighter, departures from linearity being now probably random in nature, due to experimental error or random differences in the flexing characteristics of the different compounds. It seems permissible now to fit straight lines to each graph.

The most accurate way of fitting a straight line to experimental data of this kind is by a regression technique⁷, but an alternative method is suggested which is simpler to apply. The method is illustrated in Figure 6. Two lines, X and Y, are drawn, parallel to the time axis, and located exactly midway between the pinhole and small crack levels and between the medium crack and deep crack levels, respectively. Two points of intersection are thus obtained on each graph. These points are joined by a straight line, shown dotted in Figure 6, which is produced to cut the small crack and deep crack levels. The dotted line indicates the mean cracking properties of the compound, which may be defined by two points, *viz.*:

1. The flexing time corresponding to the pinhole stage which may be called the *corrected time to pinholes*, and is a measure of the rate of crack initiation.
2. The flexing time corresponding to the deep crack stage, which may be called the *corrected time to deep cracks*.

The difference between (2) and (1) give the corrected time of propagation of the cracks from the pinhole to the deep crack stage. Alternatively, therefore, the flexing characteristics may be defined by: 1. Crack initiation time, and 2. Crack propagation time. The results so obtained for the four compounds of Figure 6 are as follows:

	Crack initiation time	Crack propagation time
Compound 1	13 hours	43 hours
Compound 2	28 hours	67 hours
Compound 3	32 hours	73 hours
Compound 4	40 hours	96 hours

The ratio of the time of propagation to time of initiation gives another method of comparing the compounds:

	Ratio
Compound 1	3.31
Compound 2	2.40
Compound 3	2.29
Compound 4	2.40

Compounds 2, 3, and 4 are similar in characteristics, although they vary in the time of crack initiation, but the variation in rate of initiation gives a similar variation in time of propagation. Compound 1, however, has a relatively slow rate of propagation when compared to its rate of initiation. The variation in the relative propagation and initiation rates is not very marked in the case of the four particular compounds, but other cases are known in which marked variations can be found. For example, in comparison with natural rubber, GR-S compounds tend to show fairly good crack initiation time but show rapid crack propagation. It is, therefore, essential to note both properties, and the above graphical method is one of the simplest means of achieving this object.

SUMMARY

In general, flexing tests are subject to large errors, some of which have been studied using a test of the du Pont belt type. An improvement in the standardization of the test conditions can be effected by using a suitably designed belt balance arm and regularly adjusting the length of the belt. The rate of cracking and also the reproducibility of the results is affected by the design of the test-piece and also by the type of fastener used.

Although the error between the results on replicate test-pieces is extremely large, more important, are the large errors due to lack of reproducibility of replicate molded slabs, and this variability probably arises during vulcanization. Extremely large differences can also occur between nominally identical repeat experiments. This may be due to differences in the judgment of the stages of cracking in different experiments. Graded photographs were found not to be of any value in improving the reproducibility of results between two different operators. Attention is drawn to the differences in types of cracking obtained with the du Pont and De Mattia test-pieces. It is pointed out that with the du Pont test-piece the cracking tends to develop in depth more than is the case with the De Mattia, and therefore it is more difficult to construct or use graded photographs with the du Pont test. Accepting the fact that variations in the disposition of the stages of cracking do occur between two different experiments, a method of treating flex-cracking results graphically is suggested. By this method random variations in results are ignored and the average flex-cracking results obtained. It is suggested that flexing properties may be defined by two characteristics, viz., (1) Crack initiation time, and (2) Crack propagation time, and an example of the method of determining these characteristics is given.

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CONTRIBUTION TO THE PHYSICAL CHEMISTRY OF HEVEA LATEX *

I. METAL CATIONS IN LATEX

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Our knowledge of Hevea latex is still incomplete, and some problems, such, for example, as a study of its natural inorganic ingredients, have not been attacked. Some work of value has been done on the analysis of the ash from latex and on the influence of metals in solution on the colloidal stability of latex, but few facts are available concerning the physico-chemical state of these metals in the natural emulsion and their partition between the serum and rubber particles.

The investigation which is described in the present paper is devoted to metal components which are capable of influencing, when in soluble form, the colloidal behavior of latex. These include potassium, sodium, calcium, and magnesium and, under some conditions, iron. Copper and manganese were not studied in this work for they have been the object of numerous investigations, and these metals play in effect the part of powerful prooxygenic agents in the oxidation of rubber.

MINERAL COMPONENTS NATURALLY PRESENT IN LATEX

The identification and study of the mineral components present in latex have not been pursued to any great extent. In 1920, de Vries¹ wrote that "The exact composition of the ash of latex, the changes in its mineral components brought about by external factors, and the partition of these components between the serum and the rubber itself are not well understood".

Some published works report that the inorganic elements most frequently found in latex are potassium, sodium, calcium, magnesium, rubidium, manganese, copper, silicon, sulfur, and phosphorus. In 1913, Beadle and Stevens² found in raw rubber 0.4 per cent potassium oxide, 0.02 per cent magnesium oxide, 0.01 per cent calcium oxide, and 0.008 per cent sulfuric acid. In 1922 Bruce³ published an analysis of the ash of a Ceylon latex. His results are given in Table I.

An examination of the results for crepe shows that the preparation of rubber changed the proportions of the ingredients. The proportions of calcium oxide, magnesium oxide, and phosphoric anhydride increase, while those of potassium oxide, sodium oxide, and sulfates decrease. It may be assumed that these latter are present in the serum of the original latex, and that the former are bound to the rubber particles.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Revue Générale du Caoutchouc*, Vol. 26, No. 5, pages 341-345, May 1949, and No. 7, pages 505-508, July 1949. This work comprises extracts from a doctorate thesis at the University of Paris, which was prepared at the French Rubber Institute and was submitted to the University on November 24, 1947. The author is at present connected with the Research Service of the Indochina Society of Hevea Plantations.

TABLE I
PERCENTAGES OF THE ASH

Component	Latex	Crepe
CaO	8.7	16.4
MgO	5.8	6.2
K ₂ O	43.0	23.4
Na ₂ O	12.4	8.9
P ₂ O ₅	24.0	43.0
SO ₃	2.8	1.4
Iron	0.7	6.7
Insoluble	2.6	—

Some years later, Rae⁴ published a complete study of the chemical composition of latex at different times of the year. He observed a relation between the proteins, potassium oxide, and phosphoric acid, which show the same seasonal changes. Flint and Ramage⁵ used the spectrographic method in analyzing the ash of latex.

Table II shows the results obtained. The average percentages of potassium, sodium, iron, calcium, and copper thus found in ordinary latex and in latex con-

TABLE II

Metal	Mean value	Extreme values	
Calcium	0.002	0.001	0.004
Magnesium	0.001	0.001	0.003
Potassium	0.2	0.2	0.5
Sodium	0.007	0.001	0.015
Iron	0.006	0.003	0.012
Copper	0.0002	0.0002	0.0005
Rubidium	0.002	0.0007	0.004
Manganese	trace	.90	0.0001

centrated by creaming suggest that sodium, calcium, and copper are associated with the rubber particles and iron and potassium with the serum. Flint and Ramage compared all these results to those obtained by present analytical methods. The amounts of potassium, calcium, and sodium found in the two cases are of the same order.

By means of the microchemical method we obtained at the French Rubber Institute the results given in Table III.

TABLE III

Latex	Potassium	Sodium	Calcium	Magnesium	Iron
A	0.148	0.0463	0.00350	0.00290	0.0011
B	0.223	0.0910	0.0151	0.0000	0.0064
C	0.123	0.0229	0.00785	0.00203	0.001
D	0.187	0.103	0.00242	0.0012	0.0008

These analyses were obtained with plantation latex both in its original form and when preserved with ammonia. Samples A, B, and C were obtained from Cochinchina, and sample D from the Cameroons.

INFLUENCE OF MINERAL INGREDIENTS ON THE COLLOIDAL BEHAVIOR OF LATEX

The stability and colloidal behavior of latex depend on the protein layer which is adsorbed at the surface of the dispersed particles. The protective action of these proteins is manifest in two different ways: (1) their dissociation

imparts to the particles, a charge the nature and intensity of which vary with the pH value, and (2) their power of hydration confers to these particles a certain degree of solvation.

From the above, one would conclude that latex is a lyophilic sol, since it owes its colloidal character to a lyophilic substance. However, experience shows that latex resembles suspensoids in certain respects. Table IV shows the similarities existing between latex and suspensoid and emulsoid sols. Latex is a mixed sol, possessing properties common to both suspensoids and emulsoids. The charge on the particles and solvation of the particles are necessarily simultaneous, for neither one alone insures stability without the other.

Metallic salts in solution modify both these factors. Henri⁶ in 1906 was the first to point out the analogy between the behavior of latex and of colloids in general on the one hand, and that of electrolytes on the other. He observed that carefully dialyzed latex flocculates but does not completely coagulate under the influence of acids.

Kemp and Straitiff⁷ and van Gils⁸ made corresponding observations about the properties of dialyzed and undialyzed latex. They noted that dialysis

TABLE IV

Suspensoids	Emulsoids	Latex
Stable when charged	Stable even when not charged	Stable when charged
Stable when dilute	Stable even when concentrated	Stable even when concentrated
Irreversible coagulation	Reversible precipitation and dispersion	Irreversible coagulation
Optically heterogeneous	Optically almost homogeneous	Optically homogeneous
In many cases colored	In most cases colorless	White
Migration in an electric field	No migration in an electric field	Migration in an electric field
Not viscous	Viscous	Viscous
Do not form gels	In many cases form gels	Do not form gels

lowers the pH value at which coagulation is brought about by the addition of an acid. This clearly shows that the action of salts and of acids on the electrokinetic potential are identical and additive.

Van Gils showed an important consequence of the presence of alkaline earths in latex. It is possible to coagulate fresh latex by the addition of soaps. The author observed that dialyzed fresh latex is insensitive to the action of soaps; on the other hand, if one adds calcium or magnesium it coagulates. The mechanism is this: insoluble calcium and magnesium soaps are formed, which are strongly adsorbed at the surface of the rubber particles and displace the proteins. The electric charge is reduced and coagulation takes place. Spontaneous coagulation of fresh latex on the plantation is explained in the same way. Van Gils thought that the complex lipides of the latex, phosphatides, and lecithides are hydrolyzed by the enzymes, with formation of insoluble magnesium and calcium soaps, which cause coagulation.

Metallic salts are capable of lowering the electrokinetic potential to its critical value, and of coagulating the latex. Henri observed that salts of the monovalent metals, sodium and potassium, do not produce any flocculation, irrespective of the amount added. Salts of the divalent metals, calcium, magnesium, and barium, added in sufficiently large proportions, cause an agglutination of latex. Salts of the heavy metals, manganese, nickel, cobalt, zinc, iron, copper, lead, and aluminum, produce flocculation at lower concentrations than in the case of alkaline earth salts.

As for the determinant effect of the valence of the ions on their coagulating power, the coagulation of latex seems to be subject to the Schulze-Hardy rule of valences. Although latex cannot be flocculated by alkaline salts, it is no less certain that the latter are capable of profoundly changing the electrokinetic potential and stability of latex. Latex preserved in ammonia is less susceptible to the action of electrolytes than is fresh latex. This is attributable to the stabilization of the proteins by the introduction of hydroxyl ions.

However, none of these facts explains satisfactorily the mechanism by which the presence of metallic salts in solution in the serum affects the nature and charge of the surface layer of the particles. It is well known that the alkali metals and the alkaline earths are naturally present in latex, but we know almost nothing of the form in which they occur, or the compounds which are capable of forming with complex organic anions present in the natural emulsion.

It is possible to formulate a large number of hypotheses: whether these metals exist in slightly dissociated organic complexes or are ionized; whether the salts or compounds are in true or colloidal solution; whether they are present in the serum, or adsorbed on the surface of the particles. Probably all hypotheses are correct, but to an extent dependent on the nature of the metal and of the latex in question. These facts are particularly interesting because they make it possible to explain the mechanism of coagulation by salts. Van Gils has shown that the phenomena of adsorption play a very important role in the flocculation of latex.

This aspect of the question has received very little attention; consequently we thought that systematic experiments might lead to some interesting results. It is easy to measure, in latex, the adsorption of metals in solution; in particular, it is possible by means of the ultracentrifuge technique to separate the serum particles and to determine them microchemically in each phase⁹.

On this basis, this work was divided as follows: In the first part the potassium, sodium, calcium, magnesium, and iron in the latex was determined by the micro-method. In the second part, the latex was ultracentrifuged, and the partition of the metals between the serum phase and the rubber phase was determined by the same methods described in the first part of the work.

THE METHODS USED FOR DETERMINING THE METALS IN THE LATEX

DESTRUCTION OF THE ORGANIC COMPONENTS IN THE LATEX

It is generally necessary to destroy the organic substances before the inorganic components of the biologic substances can be determined. In the case of latex in particular, preliminary mineralization is indispensable. It can be carried out by the wet method, by destroying the organic matter in a mixture of oxidizing acids, or by the dry method, by simply incinerating the sample in a muffle furnace. Neither of these procedures is perfect; even if the dry method is satisfactory for metals which are not in danger of being lost during incineration, *i.e.*, potassium, sodium, calcium, and magnesium; the use of a nitroperchloric mixture is preferable in the case of iron.

The following are the procedures which were followed for each method.

Dry method.—The latex specimen (5 to 10 grams) is weighed in a glass crystallizing dish about 6 cm. in diameter, and then dried in an oven at 70° C. The film is then removed carefully and put in a platinum crucible. The latter is placed in a cold muffle furnace. The temperature is then raised slowly, so as

to avoid any ignition up to 550°C . When the ash is free of carbon particles, it is dissolved in 12 cc. of 6 *N* hydrochloric acid. The crucible, covered with a watch glass, is left on a boiling water bath for 30 minutes. The contents, transferred quantitatively into a graduated 10 cc. vial, are diluted to the graduated mark.

Wet method.—From 3 to 5 grams of latex is put in a tall 250-cc. beaker and 10 cc. of concentrated nitric acid is added, with constant agitation. The beaker is covered with a watch-glass and slowly heated on a sand bath to about 150°C . The reaction is violent, but the height of the beaker is enough to prevent any loss. When effervescence ceases, heating is continued at a gentle boil. When the rubber is completely dissolved, there are added 1 cc. of concentrated sulfuric acid and 2 to 3 cc. of a mixture made up of 10 cc. concentrated nitric acid (d. 1.38) and 10 cc. of perchloric acid (d. 1.62). The beaker is covered with a watch glass and boiling is continued gently. The nitric-perchloric mixture is added in small fractions of 1 to 2 cc. until the liquid is decolorized. When the action is complete, the solution is evaporated almost to dryness, and is then diluted to a known volume for use in the subsequent determinations.

DETERMINATIONS

Determination of potassium.—Potassium can be determined by a very sensitive method which is based on the fact that dipicrylamine (hexanitrodiphenylamine) has the property of forming with potassium ions a slightly soluble salt of an orange color, which can be determined colorimetrically. Hexanitrodiphenylamine is a weak acid; the reagent used is its magnesium, sodium, or lithium salt in 3 per cent aqueous solution. Precipitation must be carried out with a very small volume. In practice, the solution to be analyzed is evapo-

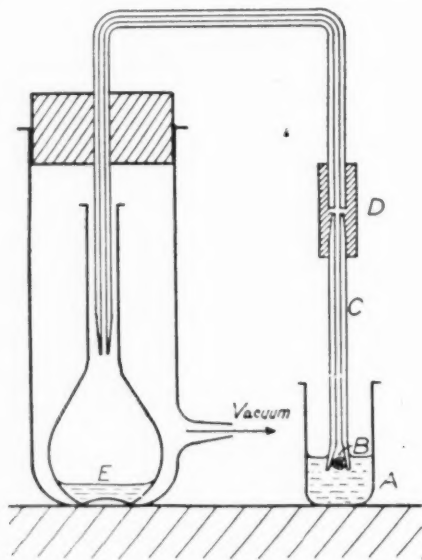


FIG. 1.—Microfiltration assembly for the separation of small quantities of precipitate.

rated to dryness, and the residue is treated with several drops of the reagent; precipitation is complete within 15 minutes.

The solubility of the precipitate increases rapidly with the temperature; in order to eliminate this source of error the reagents are saturated, at the temperature of the experiment, with potassium dipicrylamine. The excess reagent is separated from the precipitate by means of the microfiltration assembly shown in Figure 1.

The capillary tube is flared at its lower end so that a small asbestos plug can be inserted; because of the small internal diameter of the tube, the drops of liquid are completely entrained. The filtrate is collected quantitatively in the flask placed in position E. Each suction enables the precipitate to be carried to dryness, which is not possible with centrifuging. Washing is carried out

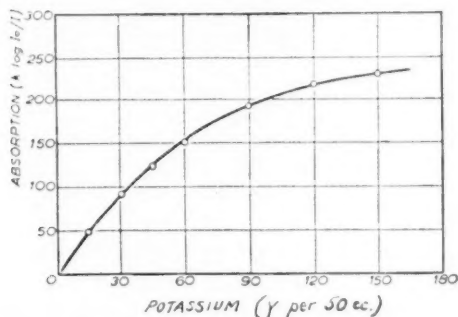


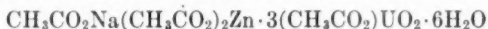
Fig. 2.—Luminous absorption curve of potassium dipicrylamine at 420 mμ.

with 12 drops of saturated potassium dipicrylamine solution; the capillary tube is divided in two parts, united by a rubber joint; the lower part, which is detachable, can be used as an agitator when the precipitate is redissolved and a volumetric determination is to be made.

The precipitated potassium dipicrylamine is dissolved in acetone. The orange red color of the solution can be measured easily in a photoelectric colorimeter. This solution shows maximum absorption for a wave length of 400 mμ. The standardization curve in Figure 2 was determined with solutions of variable concentration, using a blue-violet screen ($\lambda = 420 \text{ m}\mu$)¹⁰.

DETERMINATION OF SODIUM

Zinc or magnesium uranylacetate is at present the most widely used reagent in the quantitative determination of sodium. The latter is precipitated in the form of the triple acetate of uranyl, zinc, and sodium, having the composition:



Precipitation takes place in an acetic acid medium; it is absolutely necessary to take special precautions for this precipitation to be quantitative. The solution of precipitating reagent must be concentrated (about 40 per cent) and saturated with triple acetate at the precipitation temperature. The volume of the solution to be analyzed must be less than 0.5 cc. because of the solubility in water of the triple acetate. Precipitation is very slow; at least a half hour

should be allowed before the precipitate is separated from excess of reagent. This separation is effected by filtration, using the same apparatus as for the filtration of potassium. The precipitate is washed with ethyl alcohol saturated with triple acetate and then with pure acetone. The triple acetate is soluble in water and the solution is yellow; this coloration can be measured, but it is more advantageous to add a reagent which is capable of intensifying the color of the uranyl ion.

Rosenheim and Daehr¹¹ observed that hydrogen peroxide added to a solution of uranyl ions, buffered with a mixture of ammonium carbonate and ammonia, produces a color varying from intense yellow to red, according to the concentration of uranium. The optimum wave length for photometric measurements is about 420 m μ . The law of Beer is applicable for a large part of the curve (Figure 3). The color is stable for several hours and is specific in the case of latex.

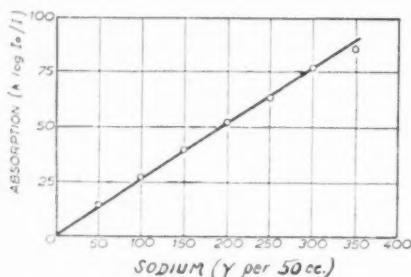


Fig. 3.--Luminous absorption curve of the uranium complex at 420 m μ .

DETERMINATION OF CALCIUM

The micro-determination of calcium, which is based on precipitation of its oxalate, is the most widely used in the study of biological substances. Its use in the analysis of latex is particularly satisfactory.

The precipitation of calcium oxalate is selective only within well defined pH values; if the pH value is higher than 6, the magnesium may be coprecipitated. When precipitation takes place in a slightly acid pH medium, separation is effected under optimum conditions. The precipitated calcium oxalate is separated by microfiltration. The asbestos must be chemically neutral, must be washed with fuming nitric acid, and then must be rinsed thoroughly with distilled water and heated in a furnace for 24 hours at 350°. As for the determination of the oxalate precipitated, the colorimetric method has not been found to be sufficiently accurate, and it is more practical to determine calcium oxalate by the manganimetric method, using the iodine-starch color change to determine the end point, according to the method of Velluz and Deschazeaux¹². Since sulfuric acid has a tendency to reduce the permanganate appreciably, titrations are carried out in perchloric medium.

DETERMINATION OF MAGNESIUM

Small quantities of magnesium can be determined colorimetrically by the thiazole yellow method.

The reagent, also called titanium yellow, is the sodium salt of dihydrothio-*p*-toluidinesulfonic acid. It is soluble in water, giving a yellow solution, but in

the presence of colloidal magnesium hydroxide, the dye is absorbed on the micelles and the color becomes rose. The pH value must be 12. Measurements are carried out within limits of concentration where the magnesium hydroxide is in colloidal solution, i.e., less than 4 mg. per liter. The optical density is measured by means of a luminous radiation beam of light transmitted in the yellow but absorbed in the red; the optimum wave length is about 550 m μ . In order to obtain results of satisfactory precision, the measurements must be made with a solution at least 40 mm. thick. When in too alkaline solution (pH 13), the calcium ion may give an orange color; it does not interfere at less than 100 mg. per liter; the addition of sucrose prevents this interference.

In the case of latex, iron interferes with the measurements, for the precipitation of ferric oxide masks the color. We have tried to avoid this separation by forming a colorless complex of the iron, but oxalic and hydrofluoric complexes of iron are not stable at the pH value used in the determination, and the addi-

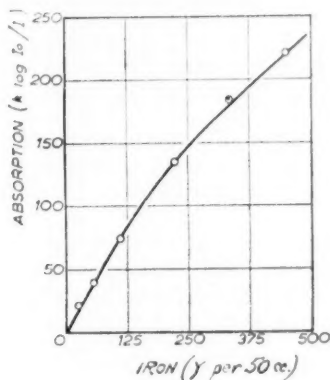


FIG. 4.—Luminous absorption curve of ferrous *o*-phenanthroline at 520 m μ .

tion of tartrates hinders the formation of magnesium hydroxide. We then considered separating the iron by means of cupferron (nitrosophenylhydroxylamine). With this reagent, iron gives a compound which is insoluble in very dilute acids (pH 2.5); separation is very easy, since the hydrochloric solution of the ash of latex already has a pH value requisite for the precipitation.

DETERMINATION OF IRON

Iron gives numerous colored reactions, some of which are sufficiently sensitive for precise quantitative measurements. We call particular attention to the use of the reaction of thiocyanate of Dufraisse and Vieillefosse¹³ in the determination of small quantities of iron in crude rubber.

Another method, the reaction with orthophenanthroline, has proved in recent years particularly satisfactory in the rapid determination of small quantities of iron in biological substances¹⁴.

Orthophenanthroline gives with ferrous iron an orange red color, the intensity of which is independent of the pH value within the range of 2 to 9. The color does not depend on the excess of reagent, and follows the law of Beer (see Figure 4). Hydroquinone, in a 5 per cent aqueous solution, was chosen as the

reducing agent of iron rather than hydroxylamine hydrochloride, which reacts more slowly. The reduction of the iron and the formation of the ferrous compound take place at a pH 4 value.

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II. ADSORPTION OF METALLIC CATIONS ON THE SURFACE OF LATEX PARTICLES

DISTRIBUTION OF ALKALI METALS, ALKALINE EARTH METALS, AND IRON BETWEEN THE TWO PHASES OF LATEX PRESERVED WITH AMMONIA

Latex was submitted to ultracentrifugation in a Huguenard-Henriot apparatus. In a few minutes a clear serum and a cream thick enough to be separated without any danger of dispersion were obtained.

Analysis gave the results shown in Table I.

TABLE I
PERCENTAGES OF METALS IN THE SERUM AND ADSORBED IN THE LATEX

Latex Metal	A		B		C		D	
	In serum	Adsorbed	In serum	Adsorbed	In serum	Adsorbed	In serum	Adsorbed
Potassium	97.3	2.7	100.7	—	90	10	88.8	11.2
Sodium	95.3	4.7	92.4	7.6	86.7	13.3	85.65	14.45
Calcium	68.6	31.4	96.1	3.9	74.6	25.4	57.9	42.1
Magnesium	64	36	100	—	100	—	98.4	1.6
Iron	—	—	89.3	10.7	97.6	2.4	99.1	0.9

These values show very important differences in the adsorption values of various latexes and show that potassium and sodium are present for the most part in the serum. The adsorption of calcium is much less. The results in the case of iron and magnesium are less significant. In the case of latex preserved with ammonia, iron is present in the form of sulfide and hydroxide in suspension in the serum. These compounds, as well as ammonium magnesium phosphate, settle rapidly during ultracentrifugation. The results above show that the alkali metals are proportionately less adsorbed than the alkaline earth metals at the rubber-water interface.

Consequently, it is natural to suppose that ions possessing two positive charges have a stronger tendency than monovalent ions to become bound to negatively charged particles. However, up to the present time there has been

no information to indicate what is the nature of this adsorption or whether there is an equilibrium between the dissolved and the adsorbed fractions.

We thought, therefore, that the dilution of latex with pure water might provide some useful data in this respect. In fact, measurements of the changes in the quantities adsorbed confirmed the existence of the equilibrium which we merely assumed before.

The latex was diluted with 0.5, 1, 2, 4, 6, 8, and 10 parts by weight of pure water, and the adsorption was measured for each dilution. Curves 1 and 2 show the desorption of potassium, sodium, and calcium. This is very clear in the case of the alkali metals. Only half the calcium is desorbed. Application

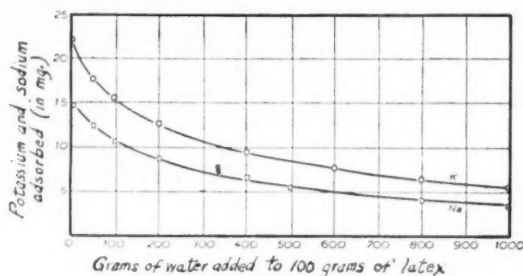


FIG. 1.—Desorption of potassium and sodium.

of the equations of Freundlich and of Langmuir to the results obtained with calcium shows that, during the dilution of latex, desorption of calcium is abnormally small, and finally becomes almost negligible with a dilution of 1 to 8. All indications are that part of the calcium was very strongly bound on the surface of the rubber particles. The nature of the adsorption of calcium is, then, at least to some extent different from that of alkali metals. Besides, determinations of nitrogen, made under identical conditions on the dispersed phase, showed that the protein layer which encloses the rubber globules is practically unaffected by dilution of the latex when this dilution does not exceed 1 to 10. One might suppose that part of the calcium adsorbed is present in a slightly dissociated protein state. This observation, in conjunction with the findings of van Gils, warrants the assumption that the "fixed" part of the cal-

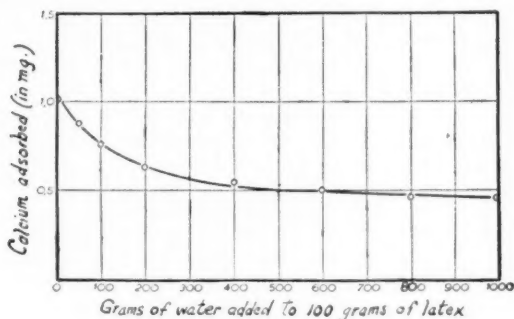


FIG. 2.—Desorption of calcium.

cium originates in its combination in a slightly ionizable form with organic substances—soaps and proteins, which are themselves strongly adsorbed by the rubber particles. In the case of alkali metals, whose compounds are more dissociated, electrosorption is the dominant factor.

ADSORPTION OF ALKALI METALS AND ALKALINE EARTH METALS ADDED TO LATEX IN THE FORM OF SOLUBLE SALTS

If increasing quantities of soluble metallic salts are added to a fixed volume of latex, a secondary adsorption takes place, superposed on that already existing in the original product.

In the case of the alkaline earth metals, the latex coagulates when the salt concentration exceeds a certain value. The appearance of instability is very gradual, and the area of coagulation extends over a rather large range of salt concentrations. The measurements of adsorption are correct only if one does not penetrate too far into this region of instability.

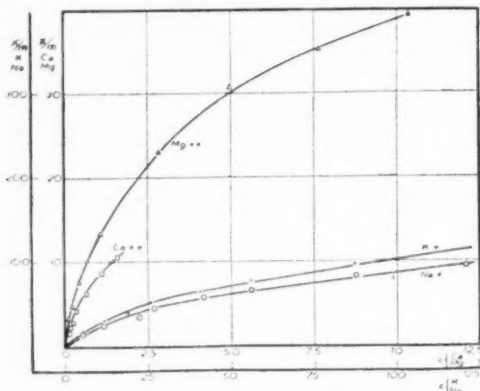


Fig. 3.—Adsorption of alkali and alkaline earth metals.

INFLUENCE OF THE NATURE OF THE METAL

Measurements made with calcium, magnesium, sodium, and potassium chlorides showed that the valence of the cation has a great influence on its tendency to be adsorbed on the surface of the latex particles.

The curves showing the adsorption values as a function of the concentration in the serum are shown in Figure 3.

For the sake of simplicity, the results are expressed in microequivalents or in abbreviation in μ equivalents. In the graphs, the quantities adsorbed are represented on the ordinate by:

$$\frac{x}{m} = \frac{\text{metal adsorbed in } \mu \text{ equivalents}}{\text{weight of the dispersed phase, in grams}}$$

and the amounts in solution by:

$$c = \frac{\text{metal in solution in } \mu \text{ equivalents}}{\text{weight of serum in grams}}$$

The adsorption of alkaline earth metals is considerably greater than that of alkali metals. This observation, frequent in colloid chemistry, shows that in this respect latex resembles suspensions.

INFLUENCE OF CONCENTRATION OF RUBBER IN LATEX

It is known that the adsorptive power of a substance dispersed in a liquid medium can vary with its concentration in the system. Fodor and Schoenfeld² in particular showed that, when Freundlich's law is applied to the results, the value of the exponent n varies greatly with the quantity of carbon adsorbing agent used. In order to ascertain whether similar observations could be made for latex, we have made measurements of adsorption on samples in which the proportions of the dispersed phase were 5, 15, and 25 per cent. The adsorption of the metallic cations, in absolute terms, was found to increase in proportion to the concentration of the latex in the dispersed phase. On the other hand, if the results are expressed by the concentrations on the particles and in the serum (that is, by x/m and by c) the adsorption on a relative basis increases with increase in dilution of the latex.

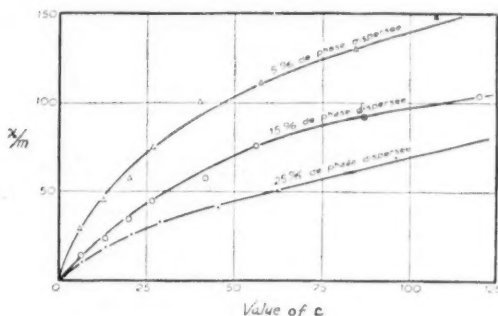


FIG. 4.—Adsorption of sodium. Influence of the concentration of rubber in the latex.

The curves of sodium (Figure 4) and of calcium (Figure 5) show clearly that dilution of latex promotes adsorption. This is quite logical, since dilution of latex by pure water promotes dissociation of the carboxyl groups of the protein layer of the particles, and, perhaps, those of the adsorbed fat acids. The negative charge on the particles increases, and with it, the tendency to absorb metallic cations.

INFLUENCE OF THE NATURE OF THE ANION

Since the dispersed particles under the experimental conditions are negatively charged, it was logical to assume that the nature of the anion had only a minor role in the adsorption phenomena. In fact, experiments performed with chlorides, sulfates, and acetates showed that the influence of the anion is slight and ill defined.

It should be noted that the correlation between the adsorption curves which were obtained experimentally and the isotherms of Freundlich and of Langmuir, with a few exceptions, is unsatisfactory. This is particularly clear in the case of the alkaline earth metals. The cause of this must be attributed to the

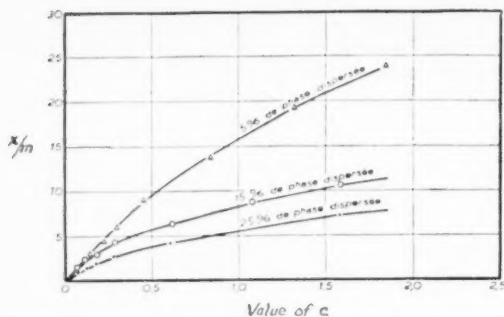


Fig. 5.—Adsorption of calcium. Influence of the concentration of rubber in the latex.

formation of insoluble soaps, according to the mechanism of van Gils. In the case of the alkaline earth metals, adsorption would correspond more closely to the theoretical equations.

COAGULATION OF LATEX BY ADSORPTION OF ALKALINE EARTH METAL IONS

It is well known that when increasing quantities of solutions of electrolyte are added to a suspensoid, the latter coagulates when the proportion of electrolyte added exceeds the "flocculation value".

This flocculation is attributable to the discharging effect of the anion when the suspensoid is positive, and to that of the cation when it is negative.

For a long time it has been assumed that the mechanism is as follows. The colloidal particle is discharged by the adsorption of the ion having an opposite charge, and flocculation occurs after this discharge. But, since Gouy³ introduced the kinetic concept of the double electric layer, it has been necessary to abandon or, to be more exact, to modify this viewpoint.

The present concept is this. The increase of the concentration in the intermicellar liquid of ions having a charge opposite to that of the micelles increases the density of the diffuse ionic atmosphere and lowers the value of the electrokinetic potential. If enough salt is added, the potential reaches its critical value and coagulation takes place.

The difference between these two interpretations of the phenomenon is very important; in the first, the discharge necessarily involves the adsorption of ions; in the second, the compression of the ionic atmosphere is manifested by adsorption. However, it is known that the ions surrounding the particles can contribute to flocculation without themselves being completely adsorbed at the molecular distance, according to the theory of von Helmholtz⁴.

Under these conditions, it is evident that measurements of adsorption at the moment of flocculation make possible only an estimation of the condensed fraction of the ions which have contributed to the lowering of the electrokinetic potential.

However, it is possible in a given system to measure for each metal a "critical adsorption" value which we shall define as being the value of the adsorption x/m at the moment of coagulation. As for Hevea latex, the critical adsorption value has no precise physical meaning. It is probable, in fact, that coagulation of latex by salts is not solely an electrokinetic phenomenon, since it is the result

in part of the adsorption of slightly dissociated soaps. Nevertheless, we shall see that, for a given latex, the measurement of the critical adsorption value for each cation under differing conditions can provide interesting data. This critical value is determined by measuring the adsorption under normal conditions at the moment of coagulation of the sample.

The resistance of any latex to the coagulating action of metallic salts depends on a number of factors, the most important of which are those which govern the intensity of adsorption of the cation; namely, the nature of the metal, the dilution of the latex, and the nature of the anion of the salt added.

INFLUENCE OF THE NATURE OF THE CATION ON THE CRITICAL ADSORPTION VALUE

Table II shows the critical adsorption values of calcium and magnesium for latexes in which the percentage of the dispersed phase is 5, 15, and 25 per cent. It is possible to draw the following two conclusions from these data.

- (1) In every case, the quantity of calcium necessary for coagulation is smaller than of magnesium.
- (2) The critical adsorption value of calcium is smaller than that of magnesium.

This shows that the particular latex which was studied was more sensitive to the coagulating action of calcium than to that of magnesium.

TABLE II

Percentage concentration of rubber in latex		5	15	25
Calcium	Q	53	63	70
	$x/m \text{ crit.}$	19.6	10.2	7.1
Magnesium	Q	262	334	375
	$x/m \text{ crit.}$	54	37	27.5

Q represents the minimum quantity of metal (in μ equiv.) required for the coagulation of 25 grams of latex.
 $x/m \text{ crit.}$ indicates the critical adsorption value.

If the theory of Freundlich and Schucht⁵ of the coagulation of salts by ions is applicable to this case, we would obtain quite similar critical adsorption values for calcium and magnesium, but this is far from being the case. Probably, however, the influence of the ions on the colloidal behavior of latex is due, not only to their charge, but also to their hydration. The magnesium ion is more hydrated than the calcium ion, and possibly the decreased potential which it provokes is accompanied by a simultaneous increase of solvation. This would explain the higher value of the critical adsorption.

INFLUENCE OF THE DILUTION OF LATEX

Examination of Table II shows that, in order to coagulate a given volume of latex, it is necessary to add a quantity of salt which is the greater, the higher is the concentration of rubber in the latex. But, conversely, the critical adsorption value increases with dilution of the latex. This is easily explained. If dilution of the latex increases the charge and as a consequence increases the electrokinetic potential, naturally a larger quantity of cations would be necessary in order to lower it to its critical value.

From these results two practical conclusions can be drawn.

(1) The yield by this process is highest when the content of dispersed phase is high. In other words, the quantity of salt required to coagulate one gram of rubber is relatively low when the latex is concentrated.

(2) When one desires to obtain rubber with the minimum possible content of metals, it is important to coagulate a concentrated latex.

INFLUENCE OF THE NATURE OF THE ANION OF THE SALT ADDED

We have already shown that the influence of the nature of the anion on the intensity of adsorption is very slight. The figures in Table III show that this is true also in the case of the critical adsorption value for a 15 per cent latex.

TABLE III

Anion		Chloride	Sulfate	Acetate
	Q	63	82	66
Calcium	$x/m \text{ crit.}$	10.2	11.5	9.8
	Q	334	410	318
Magnesium	$x/m \text{ crit.}$	37	40	37

The results obtained with chlorides and acetates are of the same order. In the case of the sulfate, the critical adsorption value appears to be slightly higher. The slight difference evident in the case of sulfate can probably be attributed, as by Scholz⁶, to the solvating action of this anion.

CONCLUSIONS

The study of latex is characterized by the fact that it is always difficult to draw any definite conclusions. One is confronted with a substance which has been synthesized by a living organism, and whose extremely complex structure is very different from that of the sols currently studied by colloid chemistry.

However, ultracentrifugation makes it possible to obtain reliable results as far as partition of the natural metallic components between the dispersing and dispersed phases is concerned.

The existence of equilibria of adsorption as a function of the dilution of latex and comparison of the experimental curves with the isotherms of Freundlich and of Langmuir shows that, in the case of latex, adsorption is not a simple phenomenon. At least two different processes seem to be involved: (1) electrosorption of the metallic cations by the negative surface of the rubber particles, and (2) indirect adsorption, whereby the metal is bound in a slightly dissociable form to an organic anion which is itself strongly adsorbed.

This would explain the much weaker adsorption of the alkali metals, which possess only a positive charge, and whose salts are in general more easily dissociated than those of the alkaline earth metals.

The results obtained for metals added to latex in the form of soluble salts lead to the same conclusions.

Measurement of the adsorption equilibria for samples of latex containing different concentrations of rubber show that, the smaller the proportion of dispersing phase to dispersed phase, the higher is the adsorption. This phenomenon, which is evident with alkali metals as well as with alkaline earth metals, can be explained by the increase of the charge on the particles when the latex is diluted. An examination of the critical adsorption values for the

different metals studied confirms the fact that the behavior of latex with salts is that of a mixed sol with both lyophilic and lyophobic properties.

These results would be more valuable if confirmed and determined more precisely by an electrokinetic study. The determination of the potential of the particles by measuring the cataphoretic velocity with respect to the adsorption of metal ions would surely permit a more accurate interpretation of the mechanism of this adsorption.

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- ¹ The dispersed phase is defined as being constituted of rubber globules and of dry adsorbed substances. The imbibed water is considered as a part of the serum. The details of the calculations by which the content of dispersed phase in any latex can be estimated are given in the Thesis.
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THE T-R (TEMPERATURE-RETRACTION) TEST FOR CHARACTERIZING THE LOW-TEMPERATURE BEHAVIOR OF ELASTOMERIC COMPOSITIONS *

J. F. SVETLIK AND L. R. SPERBERG

In recent years more and more attention has been devoted to the development of elastomeric compounds which possess superior low-temperature properties. When materials for low-temperature applications are being developed, cognizance must be taken both of their tendency to harden and to recrystallize on storage. A material may excel in resistance to freezing, but may be unsuitable because it undergoes crystallization even when stored at a temperature higher than its freezing point.

Various testing methods have been devised to measure the low-temperature properties of elastomeric materials. Since the flexibility of rubber compounds decreases at lower temperatures, many investigators have attacked the problem from the standpoint of modulus stiffening³ by measuring the modulus at several temperatures and determining the rate of hardening. The low-temperature properties of elastomeric materials can also be determined by measuring the change in elasticity at various temperatures.

In 1945 the rubber evaluation laboratory of the Phillips Petroleum Company initiated an investigation of the T-R test as a means of measuring the freeze resistance of elastomeric compounds. The T-R test is based on the principle of the T-50 test⁴, but differs in that temperatures corresponding to retractions of 0, 1, 2, 3, 5, 10, 20—90 per cent are measured rather than just the temperature corresponding to 50 per cent retraction. Yertzley and Frazer⁵ utilized a similar test for Neoprene vulcanizates, and concluded that the test was inadequate. More recently Smith *et al.*⁶ successfully applied the test, using a 250 per cent elongation.

Development work on the T-R test indicated that the test elongation is an important factor which must be considered in applying the test. This test has been utilized at variable elongations to measure the freeze resistance and at low elongations to measure the tendency of compounds to crystallize on cold storage. It has been found also that the tendency of materials to crystallize on stretching can be determined by making the determinations at varying degrees of elongation.

This report discusses the utility and versatility of the T-R test for studying the low-temperature characteristics of different elastomeric compounds. Although many rubbers have been investigated, the discussion is limited to a study of six different elastomers.

PROCEDURE

The standard Scott T-50 apparatus and individual Scott T-50 racks are utilized in the determination. The racks are marked to indicate points at

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which the sample has retracted 0, 1, 2, 3, 5, 10, 20, 30, 40, 50, 60, 70, 80, and 90 per cent of the original elongation. Distances corresponding to the various degrees of retraction are calculated using the following equation:

$$D = \frac{X}{100} (L_e - L_o)$$

where

D = distance corresponding to X per cent retraction,

X = any degree of retraction,

L_e = length of elongated specimen,

L_o = length of original specimen.

For example, a 4.0-inch specimen elongated 50 per cent to a total length of 6.0 inches must retract 0.40 inch for 20 per cent retraction:

$$\frac{20}{100} (6.0 - 4.0) = 0.40 \text{ inch}$$

Tests employing low elongations are performed with a 4.0-inch test-specimen; while tests performed in excess of 100 per cent elongation use the 2.0-inch specimen.

The test bath of the T-50 apparatus is filled with acetone or other suitable coolant, and the temperature lowered to $\pm 70^\circ \text{C}$. Specimens are fastened in the racks, elongated, conditioned in water at room temperature for five minutes, dipped into acetone (room temperature), and immediately immersed into the cold acetone bath. After the specimens are conditioned in the cold bath for three minutes, the clamps are released and the temperature is allowed to increase at a rate of 1°C per minute. Temperatures corresponding to retractions of 0, 1, 2, 3, 5, 10, 20, 30, 40, 50, 60, 70, 80, and 90 per cent are observed and recorded.

When crystallization studies are conducted, the elongated test-specimens are conditioned for a specified time interval at the desired temperature in a regulated cold box and are then transferred adiabatically to the bath of the T-50 apparatus. The procedure thereafter is identical to that employed for measuring freeze point.

EXPERIMENTAL DETAILS

The rubbers selected for this study were GR-I, Hycar OR-15, polybutadiene (prepared at 122°F), GR-S, Neoprene, and natural rubber, compounded according to the formulations in Table 1.

TABLE 1
COMPOUNDING RECIPES

Type-Elastomer	GR-I	Hycar OR-15	GR-S	Neo- prene	122° F Poly- butadiene	No. 1 Smoked sheet
Elastomer	100	100	100	100	100	100
Wyex EPC Black	50	50	50	..	50	50
Stearic acid	3	0.5	2
BRT No. 7	5	..	5	5
Zinc oxide	5	5	5	5	5	5
Sulfur	2	2	2	..	2	2
Captax	0.5
Methyl Tuads	1	0.1
Altax	..	1.25
Light calcined magnesia	7
Santocure	1.2	..	1.2	.06

DETERMINATION OF FREEZE RESISTANCE

To determine the freezing point of a stock, the T-R data are plotted as shown in Figure 1. A smooth curve is drawn through the experimentally determined points, and the body portion of the sigmoid curve is extrapolated

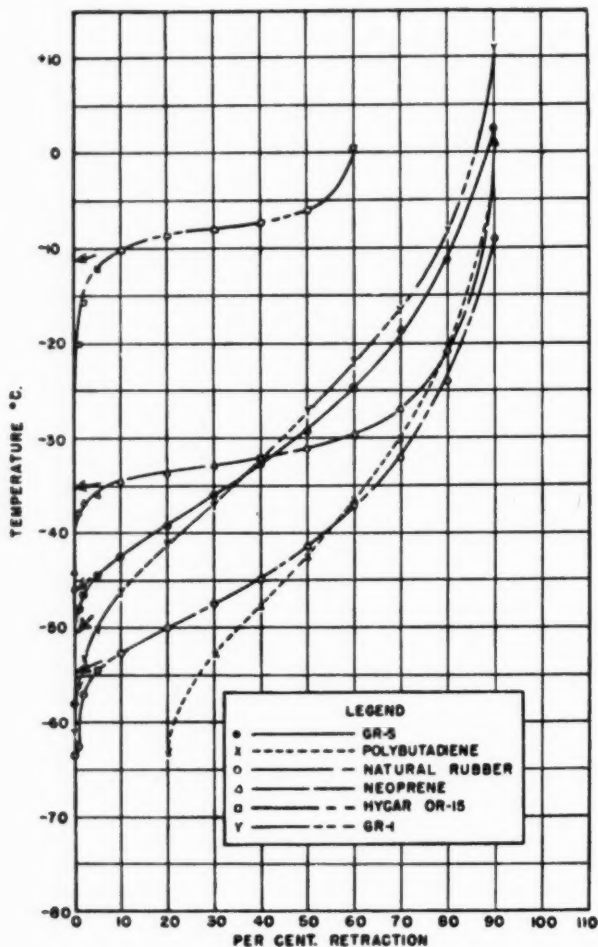


FIG. 1.—Typical temperature-reaction curves.

to zero retraction. This is the extrapolated freezing point. Good agreement is obtained when freezing point values determined in this manner are compared to results obtained by the torsion modulus technique⁷ (Table 2). These data show that the T-R test measures the second-order transition temperature of elastomeric compounds.

TABLE 2
COMPARISON OF T-R AND TORSION MODULUS FREEZING POINT VALUES

Rubber	Freezing point, ° C	
	T-R-method	Torsion modulus method
GR-I	-51	-48
Hycar OR-15	-11	-12
GR-S	-46	-45
Neoprene	-35	-39
122° F polybutadiene	-70	-79
No. 1 Smoked sheet	-55	-60

The experimental data presented in Figure 1 were determined at 50 per cent elongation. This degree of extension is preferable for freezing-point determinations because the T-R curves are somewhat easier to extrapolate than when a high test elongation is used; it will be shown in a following section, however, that the extrapolated freezing point is not appreciably affected by varying the elongation.

UTILIZATION OF THE T-R TEST TO MEASURE LOW-TEMPERATURE STIFFENING

It has been observed that a correlation exists between the retraction data of the T-R test and the degree of stiffening as determined by the torsion modulus test; i.e., the temperatures at which the samples retract 50, 20, 10, and 1 per cent correspond, respectively, to the temperatures at which the torsion modulus has increased to 2, 5, 10, and 100 times the modulus at room temperature. A correlation is shown in Figure 2, where the torsion modulus T_2 , T_5 , T_{10} , and T_{100} values are plotted *vs.* the temperature-retraction T-50, T-20, T-10, and T-1 values, respectively.

In each case the curves are displaced slightly to the left of the theoretical curves (dotted lines), which represent a perfect correlation. The results show that near the freezing point (T-10 *vs.* T_{10} and T-1 *vs.* T_{100}) the correlation is very good. These data indicate that the degree of stiffening is inversely proportional to the percentage retraction, and on this basis the reciprocal of the retraction can be used as an index of stiffness.

DETERMINATION OF CRYSTALLIZATION

Effect of elongation on materials which crystallize on stretching.—During the investigation of the T-R test method it was observed that the contour of T-R curves for different elastomers was affected by varying the elongation. This point is demonstrated in the T-R curves in Figure 3 for GR-S, GR-I, Neoprene, and natural rubber, determined at several elongations. Since the curves for Hycar OR-15 and polybutadiene are similar to those of GR-S, these are not shown. As the elongation is increased, GR-S retracts at a more rapid rate, which is evident in the greater degree of retraction at equal temperatures. GR-I differs in that the rate of retraction increases when the elongation is raised from 25 to 200 per cent and then decreases at progressively greater elongations. Natural rubber increases in rate of retraction when the extension is increased from 25 to 50 per cent and then decreases in rate of retraction as the elongation is increased further. Neoprene is relatively unaffected by varying the extension from 25 to 50 per cent, but further increases in elongation result in progressively lower rates of retraction.

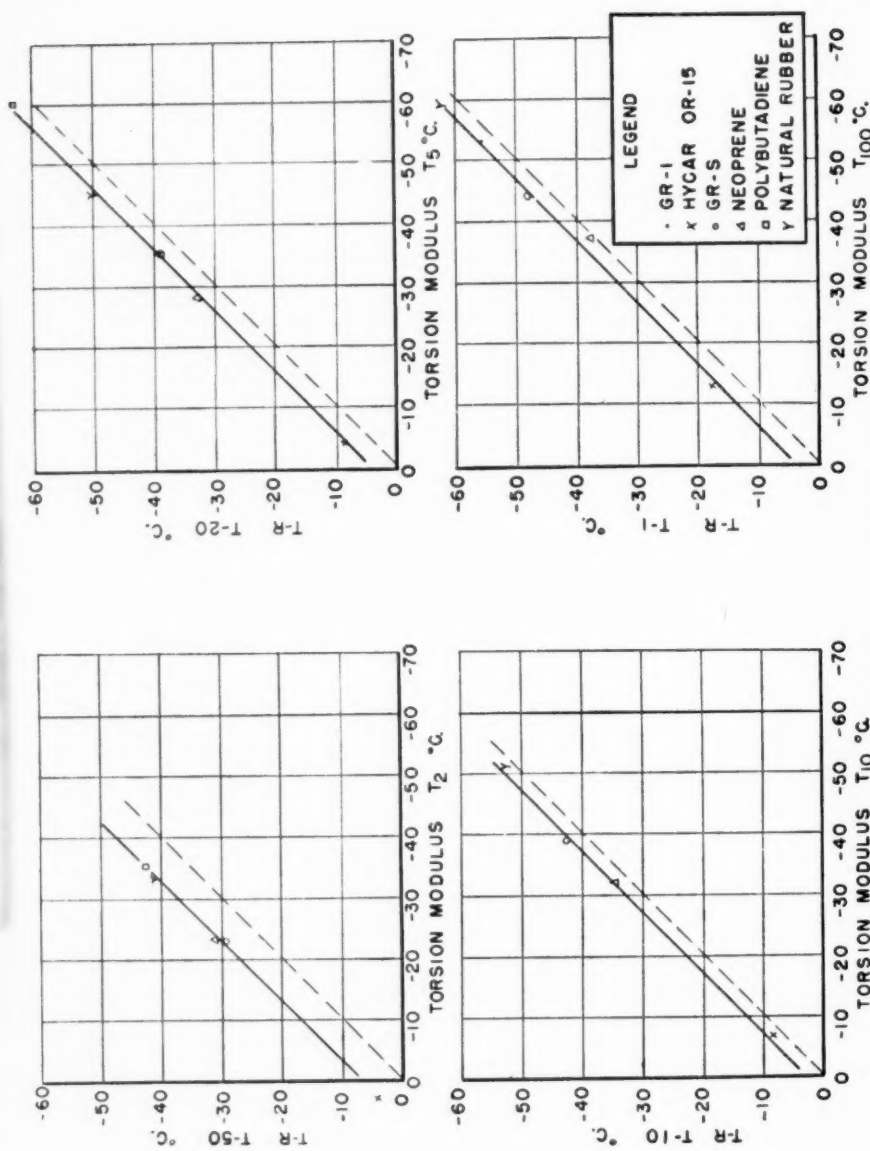


FIG. 2.—Comparison of T_2 , T_{10} , T_{20} , T_{100} values to torsion modulus T_2 , T_{10} , and T_{20} values.

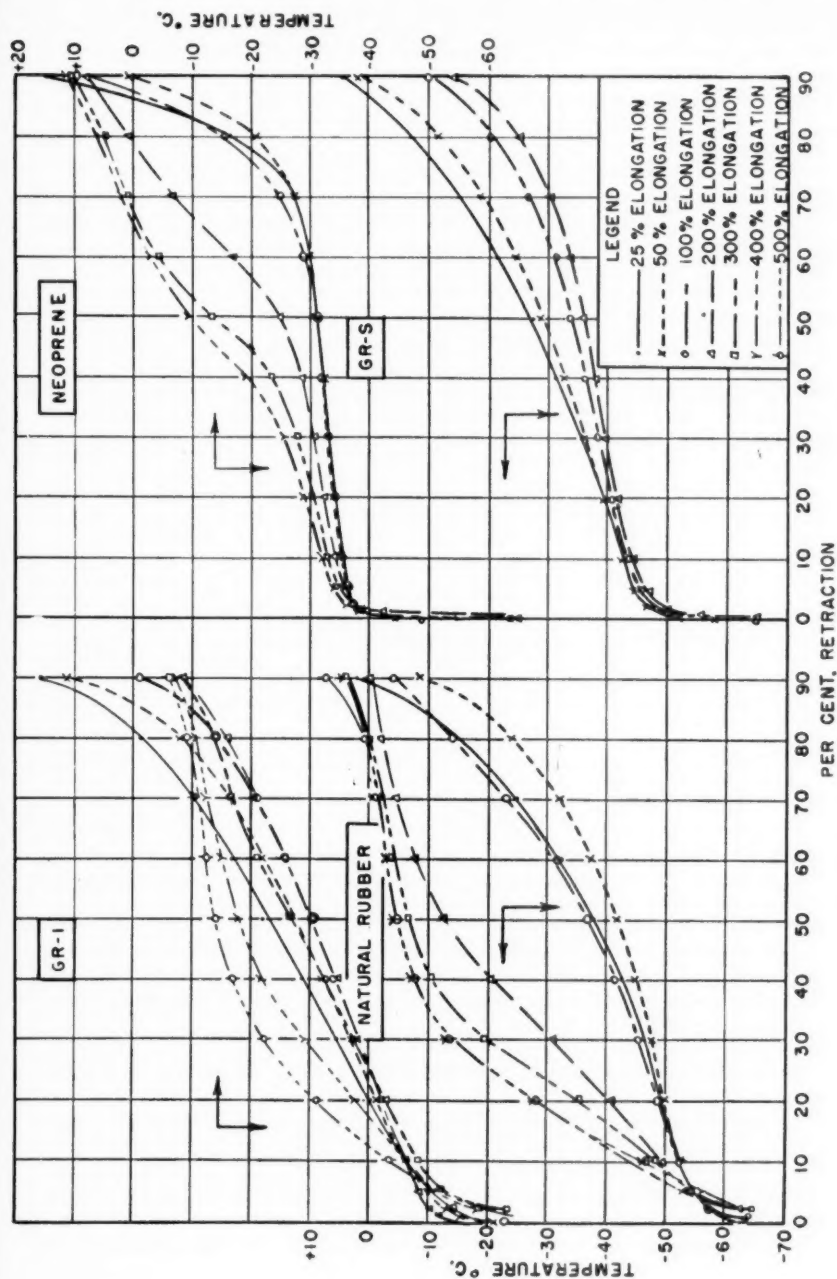


FIG. 3.—Effect of elongation on temperature-retraction characteristics.

The effect of extension is shown in another manner in Figure 4. In this plot the temperatures corresponding to various degrees of retraction are plotted as a function of the elongation. An examination of the extrapolated T-0 (temperature at 0 per cent retraction) curves for the different rubbers shows that the extrapolated freeze point values are affected only slightly by varying the extension.

Since it is known from x-ray studies and other means that natural rubber, Neoprene, and GR-I crystallize on stretching, it becomes evident that the more sluggish retraction of these materials at higher elongations is associated with crystallization, and that the T-R test can, therefore, be used to detect tendencies to crystallize on stretching if the determinations are made at a range of elongations. Since GR-S does not crystallize on stretching, no such phenomenon is observed, and the rate of retraction is increased at higher elongations because the retractive forces are greater.

Effect of low-temperature storage.—The T-R test can be utilized to detect crystallization which occurs when elastomeric compounds are stored for a prolonged period of time at a low temperature. The results of a crystallization study conducted on specimens which were elongated 50 per cent are presented in Figure 5.

GR-S, which exhibits no tendency to crystallize, is not affected by conditioning up to 72 hours at 0° F. The curves for GR-S are practically super-

TABLE 3
COLD COMPRESSION SET DATA

Rubber	Conditioning time at 0° F and 35% deflection				
	15 Hours	24 Hours	% Set	48 Hours	72 Hours
GR-I	17.8	23.2		22.2	23.9
Hycar OR-15	90.5	97.7		95.0	95.9
GR-S	20.5	22.4		20.1	20.3
Neoprene	18.5	28.1		59.0	80.4
122° F polybutadiene	15.9	20.1		20.1	17.8
No. 1 Smoked sheet	15.3	27.6		30.8	42.6

imposed, which attests to the reproducibility of the test, since determinations were made on different days. Crystallization is apparent in GR-I, Neoprene, and natural rubber in the lower rate of retraction of the conditioned specimens. GR-I shows only a small degree of crystallization after conditioning for 48 and 72 hours at 0° F. Neoprene and natural rubber, both of which crystallize more readily, show markedly lower rates of retraction of specimens which had been conditioned at 0° F before testing, and the effect is greatest for the longest conditioning cycles.

Similar data were developed for Hycar OR-15 and 122° F polybutadiene. These stocks show no tendency to crystallize, and the curves are similar to those of GR-S.

A test elongation of 50 per cent has been found to be optimum for crystallization studies. The need of this is evident when one recalls that some stocks crystallize on stretching to a high elongation, and any subsequent crystallization due to storage would be small and difficult or impossible to detect.

Cold compression set data also were determined on these stocks. The results (Table 3) show that GR-S and polybutadiene do not crystallize, and

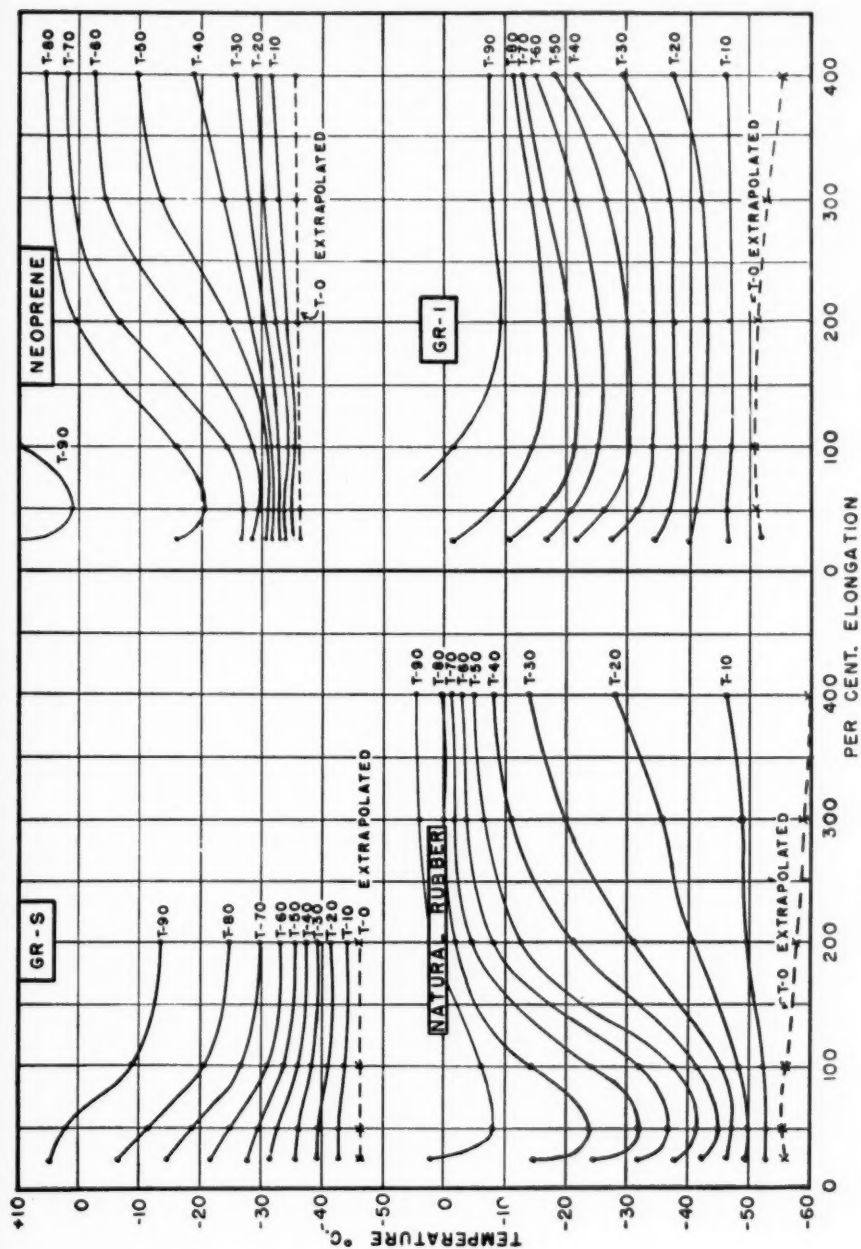


Fig. 4.—Variation of temperature-retraction T-values test elongated.

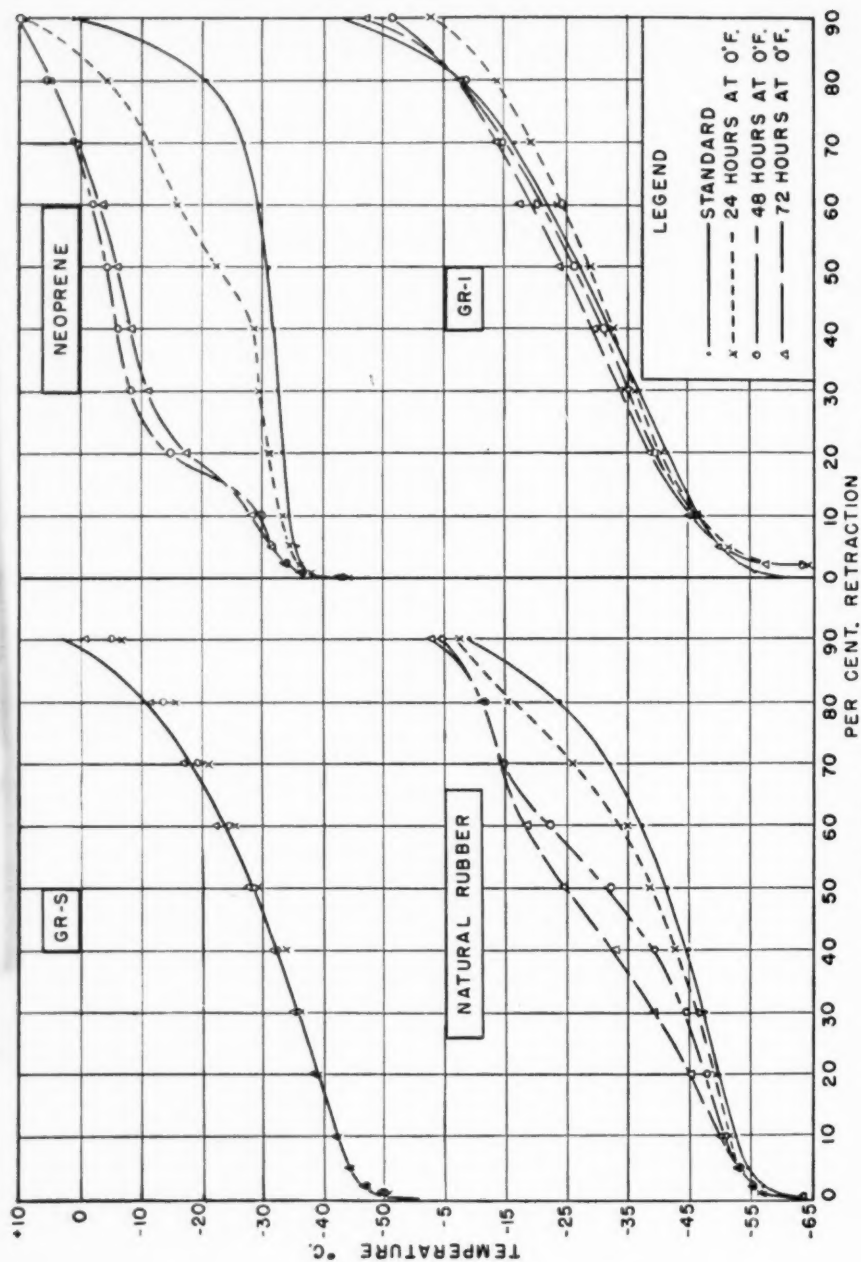


FIG. 5.—Effect of cold storage on temperature-reaction characteristics.

that the degree of crystallization of Neoprene and natural rubber increases with increased storage time at a low temperature. The Hycar OR-15 stock was completely frozen and consequently showed essentially 100 per cent set. In this respect the cold compression set test is deficient because it is not possible to differentiate between true crystallization and ordinary cold hardening or freezing.

EFFECT OF POLYMERIZATION TEMPERATURE ON CRYSTALLIZATION

Polymerization temperature exerts a significant influence on the properties of synthetic elastomers, and it has been shown by Beu *et al.*⁸ that polybutadiene prepared at low temperatures possesses some structural regularity. Since

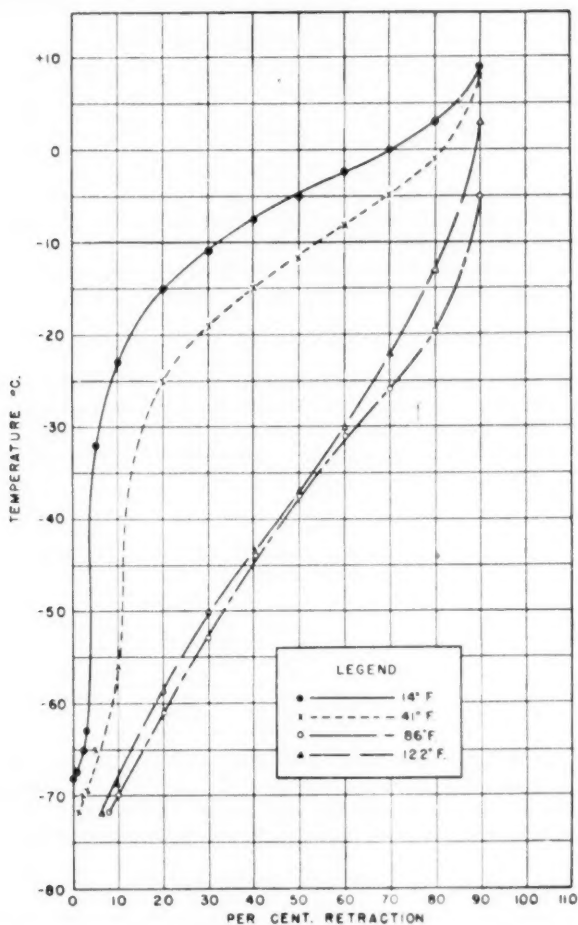


Fig. 6.—Effect of polybutadiene polymerization temperature on temperature-reaction characteristics.

elastomers which exhibit structural regularity are subject to crystallization, it was decided to evaluate the effect of polymerization temperature on the low-temperature properties. For this purpose polybutadiene elastomers prepared at 122, 86, 41, and 14° F were studied.

The T-R curves for those four elastomers compounded in a conventional tread recipe are presented in Figure 6. Polybutadiene produced at 41 and 14° F exhibits sluggish retraction characteristics, indicating a high degree of crystallization. This trend is most pronounced in the polybutadiene prepared at 14° F. These results are very significant, for they show that crystallization occurs almost immediately on exposure to the low temperature, since none of the samples received any previous conditioning.

TABLE 4
COLD COMPRESSION SET DATA FOR 122, 86, 41,
AND 14° F POLYBUTADIENE COMPOUNDS

Polymerization temperature (° F)	% Cold compression set
122	23.0
86	26.2
41	78.7
14	92.8

The cold compression set results determined on these stocks (72 hours at 0° cycle) are presented in Table 4, and the results confirm the conclusions which were reached from observing the T-R curves in Figure 6.

The freezing point of polybutadiene elastomers prepared at 41 and 14°F cannot be determined accurately from the curves in Figure 6.

ABSORPTION OF COOLANT BY TEST-SPECIMENS

Tests conducted in a liquid medium may be open to criticism on the basis that some of the test fluid may be imbibed by the specimens and thereby affect the results. The quantity of acetone absorbed by natural rubber, GR-S, and GR-I after immersion for 10 minutes at five different temperatures has been determined. The results are presented in Table 5.

TABLE 5
QUANTITIES OF ACETONE ABSORBED BY THREE RUBBERS
AT VARYING TEMPERATURES

Rubber	Temperature				
	-66° C	-40° C	-20° C	0° C	+20° C
	% Acetone absorbed				
GR-I	0.09	0.16	0.02	0.04	0.03
GR-S	0.14	0.33	0.54	1.33	3.01
Natural rubber	0.21	0.25	0.27	0.48	1.89

Only negligible quantities of acetone were absorbed by the specimens at the low temperatures. It is apparent that the absorption of acetone by the test-specimens would affect only the high values of retraction (70, 80, or 90 per cent). The effect of the coolant can, therefore, be discounted.

CONCLUSIONS

The utility of the T-R test for determining the freezing points of elastomeric compounds and their tendency to crystallize has been demonstrated. The

freezing point is not appreciably influenced by elongation, but from an operational standpoint it is preferable to employ 50 per cent extension of the sample. To determine the tendency to crystallize on cold storage a 50 per cent test elongation is optimum. To determine if a stock crystallizes on stretching the determination must be made at a series of elongations, or a minimum of two test elongations such as 50 and 200-300 per cent. Materials which crystallize almost immediately at low temperature are readily recognized. All materials which crystallize exhibit sluggish retraction characteristics, whether the crystallization is spontaneous, induced by cold storage, or by extension.

The T-R test is simple to perform, highly reproducible, and very versatile. A complete characterization of the low-temperature properties of an elastomeric compound can be made by means of the T-R test in a shorter time than by any other method or combination of methods.

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APPLICATION OF DROP ANALYSIS TO THE DETECTION OF COMPOUNDING INGREDIENTS IN RUBBER MIXTURES. II *

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One of the drawbacks of existing methods for controlling the quality of rubber products in manufacture is the lack of direct and precise chemical methods. Present methods of detection of compounding ingredients are based on physical-mechanical principles and give only an indirect indication of the presence or absence of the particular ingredients in a rubber mixture.

In our first work¹ the possibility of applying the method of drop analysis to the detection of compounding ingredients used in the rubber industry was shown. With these methods as a basis, procedures for the identification of mercaptobenzothiazole, tetramethylthiuram disulfide, magnesium oxide, zinc oxide, diazoaminobenzene, and aldol- α -naphthylamine in complex mixtures of such ingredients, but before being mixed into rubber, were developed.

The present paper describes further investigations on the application of drop analysis to the detection of such important ingredients in crude rubber mixtures as sulfur, tetramethylthiuram disulfide, mercaptobenzothiazole, diphenylguanidine, zinc oxide, and magnesium oxide.

The practical applicability of the methods described was established by repeated tests of specially prepared rubber mixtures of different compositions, and was confirmed by means of a rubber mixture containing the following compounding ingredients:

Synthetic rubber	Zinc oxide	Whiting
Mercaptobenzothiazole	Magnesium oxide	Carbon black
Tetramethylthiuram disulfide	Stearic acid	Clay
Diphenylguanidine	Caniphol	Lithopone
Sulfur	Rubrax	Magnesium carbonate
Paraffin	Neozone	

For analyzing rubber mixtures colored with organic coloring agents, special procedures are required, and they are not considered in this work.

The detection of mercaptobenzothiazole, tetramethylthiuram disulfide, sulfur, zinc oxide, and magnesium oxide is possible in the presence of other ingredients ordinarily present in rubber mixtures.

It should be noted that most of the reactions worked out by the authors in the study of mixtures of powdered ingredients are not applicable to the detection of ingredients already mixed into rubber mixtures.

The successful detection of any compounding ingredient is simplified if it can be extracted with a suitable solvent. The latter must be such that most of the substance can be extracted without affecting the other ingredients.

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from *The Industrial Laboratory (Zarodkovaia Laboratoriya)*, Vol. 15, No. 9, pages 1034-1038 (1949).

Experiments showed that, with 0.3–0.5 gram of finely divided rubber sample, approximately ten-fold the quantity of a suitable solvent at its boiling point (which must not be higher than the temp. of decompn. of the given substance) is sufficient.

An ordinary test-tube can be used for the extraction. However, even under the most favorable conditions, certain amounts of foreign substances pass into the solvent besides the substance investigated. In most cases these substances reduce the sensitivity of the drop reaction, and with certain reagents they show reactions similar to those of the ingredients under investigation. This is the greatest difficulty in efforts to find suitable reactions for the detection of ingredients which are initially extracted from the crude rubber mixture.

DETECTION OF MERCAPTOBENZOTHAZOLE

In the detection of mercaptobenzothiazole, we used the reaction described in our earlier publication, *i.e.*, the formation of a yellow bismuth salt, thus:



With small concentrations of mercaptobenzothiazole in an acid medium, the bismuth salt does not form a precipitate, but only imparts to the solution a yellow color. In the presence of bismuth hydroxide, the mercaptobenzothiazole sol is adsorbed on it at the moment of formation, and the precipitate is colored yellow. The best solvent is alcohol.

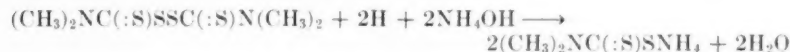
Acetone, in which mercaptobenzothiazole dissolves more readily, is less suitable, since a number of substances which are extracted from the complex rubber mixture impart to the extract a light yellow color, even in the absence of mercaptobenzothiazole.

METHOD OF DETECTION

About 0.3–0.4 gram of finely divided rubber mixture is put in an ordinary test-tube, 3–5 cc. of alcohol is added, and the whole is heated to the boiling point on a steam bath. The contents of the test-tube are boiled 5–7 minutes, with continuous agitation. The extract is transferred to a small porcelain dish and the alcohol is driven off on a steam bath. A few drops of 1 per cent sodium hydroxide solution is added to the dry residue, and the contents are very carefully stirred with a glass rod. The end of a glass capillary tube wrapped in a piece of filter paper wet in water is dipped into the mixture and the liquid is siphoned off. The liquid is transferred to a small porcelain crucible and a drop of 2 *N* bismuth nitrate is added. A yellow or orange-yellow precipitate forms in the presence of mercaptobenzothiazole.

DETECTION OF THIURAM

It is well known that tetramethylthiuram disulfide is readily converted into the dimethyldithiocarbamate. The authors have proved in particular that, in the presence of ammonium-zinc amalgam and in acetone solution, it is extremely easy to convert the thiuram into ammonium dimethyldithiocarbamate according to the reaction:



On the other hand, it is known also that dialkylcarbamates are highly reactive with copper, and the copper salts of the compounds are distinguished by their solubility in chloroform. In particular, the copper salt of dimethyldithiocarbamate $[(CH_3)_2NC(:S)S]Cu$, dissolves in chloroform and, when concentrated, the solutions are brown, and when dilute, bright yellow.

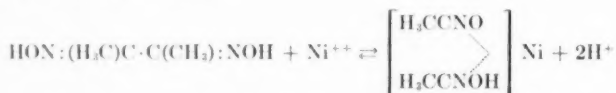
METHOD OF DETECTION

Approximately 0.3–0.4 gram of finely divided rubber mixture is put in an ordinary test-tube, 3–5 cc. of acetone is added, and the mixture is heated for 5 minutes, with constant agitation so as to keep the acetone boiling gently. A few pieces of 2 per cent zinc-mercury amalgam and 2–3 drops of concentrated ammonia are then added to the test-tube, and the whole is shaken for 2–3 minutes. The liquid is decanted into another test-tube, diluted with a little water (1–2 cc.), 5–6 drops of 1 per cent copper acetate solution and a few drops of chloroform are added, and the mixture is agitated vigorously. If stratification proceeds slowly, one-third the volume of water is added. The chloroform layer assumes an intense yellow or yellow brown color if tetramethylthiuram disulfide is present. In its absence this layer is colorless or pale yellow.

DETECTION OF DIPHENYLGUANIDINE

Burmistrov² described a reaction for the detection of diphenylguanidine which is based on its property of coloring phenolphthalein red. For the detection of diphenylguanidine in crude rubber mixtures, however, this reaction has proved insufficiently sensitive.

If a practically colorless equilibrant solution of dimethylglyoxime and a nickel salt are used as indicator:



then even an insignificant quantity of diphenylguanidine destroys the equilibrium, and thereby reduces the reddish color of the nickel dimethylglyoxime. This reaction can be applied successfully to the detection of diphenylguanidine in a crude rubber mixture. We must bear in mind that, during the extraction of diphenylguanidine from a mixture prepared from sodium-butadiene rubber, enough sodium hydroxide is extracted to color the reagent, even in the absence of diphenylguanidine. If an extract previously evaporated is again extracted with ether, then only the diphenylguanidine enters the ether solution, and it can be detected easily by means of the above-mentioned reaction.

An equilibrant solution of nickel dimethylglyoxime is prepared from a solution of 2.3 grams of $NiSO_4 \cdot 7H_2O$ in 800 cc. of water, mixed with a solution of 2.8 grams of dimethylglyoxime in alcohol. This is filtered after 30 minutes, and the filtrate, to be used as reagent, is kept in a flask with a ground-in stopper.

METHOD OF DETECTION

About 0.3–0.4 gram of the finely divided rubber mixture is put in an ordinary test-tube, 3–5 cc. of alcohol is added, and the mixture is heated for 5–7 minutes, with continuous agitation, keeping the alcohol boiling gently. The alcoholic extract is poured off into a porcelain dish and is evaporated to dryness in a

steam bath. The residue is taken up in 1-2 cc. of ether, the ether solution is poured off into another porcelain dish, the ether is evaporated, and to the dry residue is added a few drops of an equilibrant solution of nickel dimethylglyoxime, while being stirred carefully with a glass rod. If diphenylguanidine is present, the walls of the vessel are colored rose within not more than 1-2 minutes.

DETECTION OF SULFUR

Sulfur is readily soluble in pyridine and, in the presence of caustic alkalies, this solution readily forms a compound which in small concentrations is intense blue and in large concentrations is reddish brown. The reaction is so sensitive that it makes possible the detection of free sulfur without preliminary extraction, and with the use of only a few milligrams of rubber mixture.

METHOD OF DETECTION

A microtube of 1-cc. volume is one-quarter filled with pyridine, and a few drops of 2 *N* sodium hydroxide solution and a few grains of the experimental rubber mixture are added. The contents of the test-tube are carefully heated on an alcohol burner. The appearance of a blue color indicates the presence of sulfur.

DETECTION OF ZINC OXIDE

The reaction described by Kulberg³ was used to detect zinc oxide. Zinc oxide is easily extracted from the rubber mixture by the addition of acetic acid. The use of acetic acid makes possible the extraction of zinc oxide even in the presence of lithopone, as well as zinc sulfide, which is insoluble in acetic acid. It should be added that, for the detection of zinc oxide in light colored rubber mixtures, it is possible to use the reaction described by the authors in their earlier work.

METHOD OF DETECTION

0.3-0.4 gram of the finely divided rubber mixture is put into an ordinary test-tube, 3-5 cc. of 20 per cent acetic acid is added, and the mixture is boiled for 5-7 minutes, with constant agitation. The acetic acid extract is transferred to a porcelain dish and evaporated to dryness on a sand bath. The residue is dissolved, with stirring, in two drops of water and one drop of 1 per cent sulfuric acid. Then 2 drops of a solution of 0.05 gram of cobalt chloride, sulfate, or acetate in 100 cc. of water and 2 or 3 drops of ammonium mercuric thiocyanate solution⁴ is added. The rapid appearance of a blue precipitate indicates the presence of zinc oxide in the rubber mixture. Zinc sulfide present in the lithopone does not interfere with the reaction.

DETECTION OF MAGNESIUM OXIDE AND BASIC CARBONATE

The difficulties of detecting magnesium oxide in a crude rubber mixture consist in the fact that the overwhelming proportion of colored reactions of magnesium are largely suppressed by zinc salts. Quinalizarin is an exception, and its sensitivity is decreased only slightly by the presence of zinc salts. This reagent was also used in the experiments described for the detection of magnesium compounds in crude rubber mixtures. Extraction, as in the preceding case, was carried out by the addition of acetic acid.

METHOD OF DETECTION

The finely cut rubber mixture (0.3–0.4 gram) is put in an ordinary test-tube, 3–5 cc. of 20 per cent acetic acid is added, and the mixture is boiled, with continuous agitation, for 5–7 minutes. The extract is transferred to a porcelain dish and is evaporated to dryness on a sand bath. The residue is dissolved, with stirring, in a mixture of 4 drops of water and 2 drops of 1 per cent sulfuric acid solution. The liquid is filtered off by means of a capillary tube (see under the detection of mercaptobenzothiazole), the solution is transferred to a porcelain dish, 3–4 drops of a solution of 1–2 mg. of quinalizarin in 10 cc. of alcohol are added and, finally, an excess of 2 *N* sodium hydroxide is added dropwise.

If magnesium oxide is present, a blue precipitate forms. A violet or lilac precipitate has no significance.

Since the reagent itself is blue-violet in alkaline solution, in doubtful cases a control experiment should be carried out simultaneously. In this, the extract of a complex rubber mixture containing zinc oxide but no magnesium oxide is used as the control solution. Such an extract can be prepared beforehand, and used whenever necessary.

It is not possible to distinguish calcined magnesia from magnesium carbonate.

CONCLUSIONS

1. The method of drop analysis is of wide use in the testing of crude rubber mixtures.

2. Methods of detection of mercaptobenzothiazole, tetramethylthiuram disulfide, diphenylguanidine, sulfur, zinc oxide, and magnesium oxide were developed.

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- ⁴ In the preparation of this reagent, 2.7 grams of mercuric chloride and 3.9 grams of ammonium thiocyanate are dissolved in 100 cc. of water. A mixture of 1 drop of this reagent with 1 drop of cobalt solution should not give a blue residue in the porcelain dish when stirred for 1–2 minutes.

QUALITATIVE ANALYSIS OF RUBBER MIXTURES. II *

S. I. BURMISTROV

INTRODUCTION

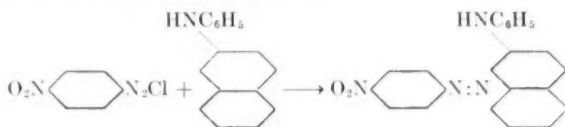
In Part I, reactions by which it is possible to identify Neozone, aldol- α -naphthylamine, tetramethylthiuram disulfide, and diphenylguanidine, when present alone or in the form of simple mixtures with inorganic ingredients, were described. These reactions can serve for the determination of these ingredients in complex mixtures as well, provided that the mixtures are first separated in the pure state. Chromatographic separation on a strip of filter paper is especially suitable for this process.

It should be remembered that it is always difficult to determine the various ingredients in finished rubber products when they have undergone chemical changes or decomposition under the influence of high temperatures.

In many cases the decomposition products have not been examined, and this naturally has hindered qualitative analysis of the mixtures. For this reason a study of the behavior of various ingredients under actual conditions of vulcanization and from this the development of methods of qualitative analysis became necessary. The author has shown that diphenylguanidine decomposes with formation of aniline under these conditions; it is also well known that diazoaminobenzene forms aniline and aminoazobenzene forms diphenylamine. In certain cases a specific ingredient can be detected by means of its decomposition products. Thus the presence of diphenylguanidine in the original mixture can be established if aniline is detected in the rubber and there are no other ingredients in the mixture which give off aniline during decomposition.

In this work methods of detecting Neozone in raw rubber, rubber mixtures, and finished rubber products and also methods of determining mercaptobenzo-thiazole, diphenylguanidine, diazoaminobenzene, and products of their decomposition are described.

In the detection of the different ingredients, highly sensitive reactions based on the formation of diazo compounds and azo dyes proved especially suitable. Most of the reactions proceed easily and simply on filter paper and are applicable for fast production control.



NEOZONE

Neozone (phenyl-2-naphthylamine) can be most easily detected by the method described of the formation, with 4-nitrophenyldiazonium chloride, of a

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from *The Industrial Laboratory* (Zavodskaya Laboratoriya), Vol. 15, No. 9, pages 1039-1042 (1949).

a reddish violet azo dye. The process of formation of the azo dye is so sensitive that Neozone can be determined by the following method. With a capillary tube, a benzene solution of 4-nitroaniline (containing 1 mg. per cc.) is drawn as a stripe across a piece of filter paper 7-8 mm. wide and the benzene is evaporated. Then the paper is successively treated with hydrogen chloride vapor and alkyl nitrite vapor for 3-5 seconds; in this way, 4-nitrophenyldiazonium chloride forms on the paper. The experimental rubber sample, rubber mixture, or finished rubber product is heated, a drop of alcohol or acetone is applied to a freshly cut surface, and then the paper strip containing 4-nitrophenyldiazonium chloride is applied. If Neozone is present, an intense reddish violet color develops. Neozone can be detected in many rubber products by this method. Thus we detected Neozone in seven specimens of domestic synthetic rubber, in rubber stoppers, etc.

If it is necessary to detect Neozone in sponge rubber containing diazoaminobenzene, then the aminoazobenzene and aniline must be separated by chromatographic adsorption on paper. The fact that Neozone, unlike aniline or aminoazobenzene, is a very weak base, facilitates this. The finely cut rubber sample is treated with 2 cc. of alcohol while being heated. The alcohol solution is poured off into another test-tube, water is added, the mixture is made alkaline to remove acid components, and is treated with benzene. The benzene solution is chromatographed on paper. On a piece of paper, 4-nitrophenyldiazonium chloride is prepared as described above, and the location of application of the solution is marked with a pencil. After formation of the diazonium salt, the paper is again treated with hydrogen chloride vapor. Approximately 1 cm. distant from the line of 4-nitrophenyldiazonium chloride, the experimental solution is applied several times. Then pure benzene is applied and the Neozone is carried to the 4-nitrophenyldiazonium salt line. The point where the benzene mark touches the 4-nitrophenyldiazonium salt shows a reddish violet border.

MERCAPTOBENZOTHAZOLE

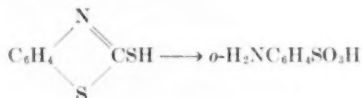
Mercaptobenzothiazole can be detected by the formation of colored salts with bismuth² or copper, or by oxidation to orthanilic acid in alkaline solution; the orthanilic acid is then detected by the diazo reaction.

Mercaptobenzothiazole can be detected by the first method only in raw rubber mixtures in the absence of tetramethylthiuram disulfide, since the decomposition products of this thiuram also give color reactions with bismuth and copper salts.

The interfering action of tetramethylthiuram disulfide can be avoided by boiling with an acid or an alkali; this decomposes the thiuram. Accordingly the experimental rubber mixture is boiled 5-10 minutes with a 5 per cent sodium hydroxide solution, the alkaline solution is filtered off, is treated with excess hydrochloric acid, and boiled until all hydrogen sulfide is eliminated. The mercaptobenzothiazole, which precipitates with the sulfur, is extracted with 0.5-1.0 cc. of benzene and the benzene solution is separated and shaken with a 0.1 molar solution of bismuth nitrate or with a 5 per cent solution of copper sulfate. In the presence of mercaptobenzothiazole, with bismuth nitrate an orange precipitate forms; with copper sulfate at first a yellow solution is formed and then a yellow suspension. We did not succeed in detecting mercaptobenzothiazole in finished rubber products by the method.

If the quantity of mercaptobenzothiazole is small, especially in finished rubber products, it can be determined by a reaction which is based on its conversion

to orthanilic acid. The mercaptobenzothiazole is oxidized by hydrogen peroxide or hypochlorite in alkaline solution and then recovered. The conversion can be represented schematically thus:



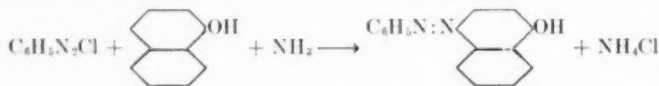
Orthanilic acid can be detected by the diazo reaction. The sample of rubber mixture or finished rubber product, finely ground with a file, is boiled in a 2 per cent sodium hydroxide solution to which a few drops of perhydrol have been added. The alkaline solution is filtered off and heated with zinc dust. After boiling for 5–10 minutes, the liquid is allowed to settle, a drop of it is put on filter paper, dried, treated successively with hydrochloric acid and alkyl nitrite vapors, a solution of α -naphthol in benzene is added, and the mixture is treated with ammonia. If mercaptobenzothiazole is present, a red color appears; this turns orange in acetic acid vapor and violet in hydrogen chloride vapor. The reaction can also be effected in solution. In this case, the liquid is filtered off from the zinc dust, acidified, and a 0.1 N solution of sodium nitrite is added until a positive reaction is produced on iodine-starch paper. The nitrite residue is removed by adding urea or aminosulfonic acid. The azo compound is best formed in acid medium with dimethyl-1-naphthylamine (reddish violet color) or α -naphthol (red color in alkaline solution). The formation of orthanilic acid from mercaptobenzothiazole proceeds so nearly quantitatively that it was not studied here. Aniline and all substances which form aniline by hydrolysis prevent this reaction. To remove the aniline before diazotization, it is necessary to evaporate the alkaline solution on a steam bath, dissolve the residue, and diazotize as described. Tetramethylthiuram disulfide does not prevent the detection of mercaptobenzothiazole in this reaction.

ANILINE

In certain cases aniline is present in finished rubber products. It can form as a product of the decomposition of diazoaminobenzene or diphenylguanidine. It is particularly easy to detect diphenylguanidine in finished rubber products by the presence of aniline, if no other ingredients which decompose into aniline are present. The detection of aniline is rendered easier by its volatility. The rubber is cut with a razor and the end of a strip of filter paper is put into the cut about 5–8 mm. After 10–15 minutes the paper is removed and treated with alkyl nitrite vapor. The paper is held for 2–3 seconds in hydrogen chloride vapor and then placed in a test-tube over a mixture of different proportions of water, hydrochloric acid, and ethyl alcohol, to which a few crystals of sodium nitrite have been added immediately before.

Treatment of aniline hydrochloride with ethyl nitrite forms phenyldiazonium chloride; thus: $\text{C}_6\text{H}_5\text{NH}_3\text{Cl} + \text{C}_2\text{H}_5\text{NO}_2 \longrightarrow \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_2\text{H}_5\text{NO} + \text{H}_2\text{O}$. The diazonium salt is detected by the formation of an azo dye with α -naphthol. For this purpose a solution of α -naphthol in benzene (2 mg. per cc.) is applied to a strip of filter paper with a capillary tube. In order to form the azo compound, the paper is treated with ammonia gas. In the presence of aniline, a sharply defined orange stain appears. In hydrogen chloride vapor,

the color of this stain changes to violet. It should be mentioned that the aniline reaction becomes weaker in the course of time.



DIAZOAMINO BENZENE

Diazoaminobenzene is used in the manufacture of sponge rubber, since it decomposes at elevated temperatures, with evolution of nitrogen gas. Aniline, diphenylamine, and aminobenzene are also formed at the same time. The detection of diazoaminobenzene in raw rubber mixtures by the method previously described¹ presents no difficulties. A large part of the diazoaminobenzene in a finished rubber product has, however, decomposed, and in addition, colored products which prevent the detection of the diazoaminobenzene are formed. It is easy to establish whether there was diazoaminobenzene in the original mixture by the presence of colored byproducts, extractable with alcohol. In certain cases, however, it is desirable to know how completely the diazoaminobenzene has decomposed. Since the presence of the latter in finished rubber products can be established only after separation of the other decomposition products, one can take advantage of the fact that diazoaminobenzene does not form salts with hydrogen chloride, although the colored byproducts of its decomposition do form such salts.

To separate the ingredients, diazoaminobenzene is extracted from rubber by boiling the latter in alcohol, making the alcohol solution alkaline, adding water, and treating with benzene. The benzene solution is applied to a strip of paper previously treated with hydrochloric acid, by means of a capillary tube. The colored compounds remain in the center, and form a rose colored area, while the diazoaminobenzene concentrates on the periphery of the benzene area. To separate the diazoaminobenzene more completely, a few drops of pure benzene are applied to the center with a capillary tube. Then a benzene solution of α -naphthol is applied, the paper is treated with hydrogen chloride gas for 10–15 seconds, and, to induce formation of the azo compounds, it is treated with ammonia gas. In the ammonia vapors a yellow color forms in the center, and on the periphery, an orange color. In hydrogen chloride vapor, a reddish color appears in the center and a violet color around the periphery.

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THE DETERMINATION OF FREE SULFUR IN VULCANIZATES BY A POLARO- GRAPHIC METHOD *

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INTRODUCTION

The determination of free sulfur in vulcanizates is one of the oldest in rubber analysis, and its accurate evaluation is important in any study of the state of vulcanization of a rubber compound.

With the introduction of sulfur-containing accelerators, etc., the original oxidation method described in standard works on rubber analysis required modification, as it gave a figure which included elementary sulfur and sulfur from other ingredients of the acetone extract. This complication led to the use of a variety of supplementary oxidizing agents, such as bromine, potassium permanganate and potassium chlorate, in conjunction with nitric acid, with the object of oxidizing completely the elementary sulfur, leaving unaffected the combined sulfur in other ingredients of the acetone extract.

Recognition of the shortcomings of the oxidation methods has led many investigators to approach the problem along fundamentally different lines. Thus Kelly¹ exhaustively extracted the acetone extract with sulfur-saturated ethyl alcohol, which, it was suggested, removed all ingredients other than the sulfur. This method frequently fails because many acetone-soluble ingredients of the rubber remain undissolved by alcohol, and also the close temperature-control necessary to ensure that the alcohol remains saturated with sulfur is difficult to attain in routine-testing laboratories.

Two other methods have received a measure of support generally and have been closely studied in this laboratory. Mackay and Avons' modification² of Bolotnikov and Gurova's method³ consists of boiling the acetone extract with aqueous sodium sulfite to convert the elementary sulfur into thiosulfate, which is then estimated by iodine titration. The method of Hardman and Barbehenn⁴, or copper-spiral method, which with slight modifications is being considered by the British Standards Institution as one of the recommended methods for the estimation of "true" free sulfur, depends on direct combination of copper and sulfur, in acetone, to form copper sulfide. The copper sulfide and its metallic support are treated with acid, and the liberated hydrogen sulfide is absorbed in cadmium acetate solution.

It seems to be generally accepted, however, that both these methods may lead to high results when certain accelerators are present. For example, it has been shown in this laboratory that tetramethylthiuram disulfide and related compounds are decomposed by metallic copper, and the copper-spiral method is, therefore, inapplicable in the presence of such accelerators.

The present method was developed in response to the demand for one which would give "true" free sulfur in the presence of readily decomposable accel-

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ators, and would be sufficiently rapid and accurate in the hands of junior assistants to serve the needs of routine testing laboratories. The publication of Proske's work⁵ on the polarographic determination of sulfur formed the starting point of this investigation. He referred briefly in this paper to the possible application of the method to the determination of free sulfur in rubber.

EXPERIMENTAL

Proske, in a later publication⁶, describes in greater detail the determination of free sulfur in rubber and recommends that separation from the vulcanizate should be effected by pyridine extraction. The solution of sulfur is then added to an acetic acid/sodium acetate buffer, and the whole is said to form a suitable base solution for the reduction of the sulfur. Methyl cellulose is used as a maximum suppressor. When Proske's procedure was followed in this laboratory, however, very poor curves were obtained, from which accurate measurement was impossible. Irregularities were obtained in the region of the decomposition potential, and a pronounced maximum was invariably produced. Proske himself admits the difficulty of dealing with this weakness. The first experiments were, therefore, concerned with modification of the electrolyte to obtain curves of more regular shape. Improvement in the shape of the curve at the decomposition potential was readily achieved by a variety of agents, but usually at the expense of an enhanced maximum. The difficulty was overcome most satisfactorily by incorporating an external calomel electrode in the cell assembly.

Eliminating the maximum proved somewhat more difficult, a wide selection of the commoner suppressors being tried without effect, although it was established that gelatin was better in this respect than methyl cellulose. In view of these results, it seemed more promising to make a more drastic change in the composition of the electrolyte. Reducing in a citric acid/ammonium citrate buffer solution, by moving the half-wave potential nearer to the electrocapillary zero, successfully removed the maximum, but the general form of the wave was less suitable for measurement, particularly for small amounts of sulfur. Methanol, however, was found very effective as a maximum suppressor, presumably because it inhibits to some extent the adsorption of ions on the mercury cathode, and subsequent work was carried out with this as an ingredient of the base solution.

Determination of n and D constants in the Ilkovic equation.—For the preparation of a calibration curve, recrystallized sulfur was used, and direct weighings were made of portions over the range 0.27 mg. to 2.66 mg. The sulfur was dissolved in 5 cc. pyridine, 10 cc. absolute methanol was added, and then 5 cc. of a buffer solution 0.35 M with respect to acetic acid and sodium acetate. It was found essential not to exceed a sulfur concentration of 5 millimol per liter in the final solution, since precipitation is liable to occur beyond this limit. A portion of the sulfur solution was transferred to a polarographic cell, dissolved oxygen removed with nitrogen while adjusting the temperature to 25° C in a thermostat, and a polarogram recorded over the range -0.3 to -1.0 v. against the saturated calomel electrode.

From a series of experimentally determined values for the diffusion current (i_d) corresponding to known concentrations (C) of sulfur over the range 0.42 to 4.2 millimol per liter (the molecular weight of sulfur being taken as equal to its atomic weight), the equation of the regression line of i_d upon C was calculated (see Figure 1).

The mass of mercury flowing from the capillary in one second was 1.781 mg. and the drop-time 3.2 seconds, from which the capillary constant $1.784 \text{ mg.}^{\frac{1}{2}} \text{ sec.}^{-\frac{1}{2}}$ is calculated.

It has been shown theoretically that a graph of $\log \frac{i}{i_d - i}$ against the potential of the dropping electrode is a straight line with a reciprocal slope of $\frac{0.059}{n}$ v. at 25°C , and that the log term has the value zero at a point corresponding to the half-wave potential of the substance being reduced. The log graph drawn from data taken from a polarogram of sulfur had a reciprocal slope of 0.063 v., which is in reasonable agreement with the theoretical value for $n = 1$, and the potential measured at the point where the log term disappears was -0.63 v. versus the saturated calomel electrode. An identical value for the half-wave potential was obtained by direct measurement from the polarogram, using the "three-tangent" method for determining wave height.

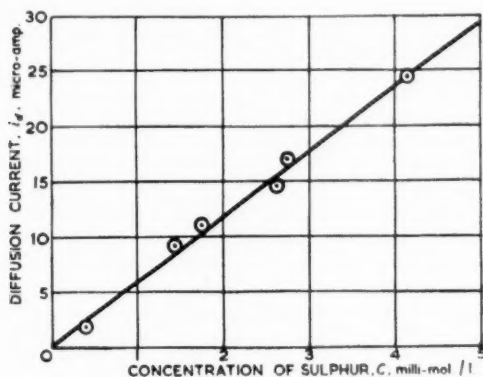


FIG. 1.

Substitution of the known terms in the Ilkovic equation then gave a value of $3.06 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$ for the diffusion coefficient of sulfur in this base solution.

Compounded rubber.—The polarographic method was compared directly with the copper-spiral method and the nitric acid-potassium chlorate standard gravimetric process⁷, using a simple natural rubber stock accelerated with diphenylguanidine. This accelerator was chosen because it contains no sulfur, and also because it has been established that it gives no polarographic wave in the pyridine/methanol/acetate electrolyte. The composition of the stock was as follows: Rubber, 100; sulfur, 3; diphenylguanidine, 1; zinc oxide, 5; stearic acid, 2. Samples from this stock were vulcanized at 138°C for 20, 40, 60 and 80 minutes to give a progressive decrease in the amount of uncombined sulfur.

Determination of the free sulfur by the copper-spiral and gravimetric methods was preceded by acetone extraction carried out according to the standard B.S.I. recommendation⁷, but in the case of the polarographic determination, advantage was taken of the smaller amount of sample required (0.1–0.2 gram) to reduce the preliminary extraction to the semimicro scale;

the time for this extraction was thus reduced to 4 hours. The extract was dried at room temperature by blowing in a gentle current of air, then warmed gently with 5 cc. pyridine, added by pipette, until the extract was completely dissolved. Ten cc. absolute methanol was then pipetted into the cooled solution, followed by 5 cc. sodium acetate-acetic acid buffer solution. After transference of a portion of this solution to the polarographic cell, dissolved oxygen was removed as before and the current-voltage curve recorded over the range -0.3 to -1.0 v. at a temperature of 25°C .

"Free" sulfur as determined by all three methods is shown in Table I.

TABLE I

Vulcanizing conditions	Nitric acid oxidation	Free sulfur (%) copper spiral	Polarographic
(i) 20 min. @ 138°C	0.98	0.95	0.98
As (i), but after standing for 14 days	0.86	0.86	0.88
(ii) 40 min. @ 138°C	0.24	0.23	0.26
Repeat of (ii)	0.26	0.29	0.26
(iii) 60 min. @ 138°C	0.093	0.092	0.078
(iv) 80 min. @ 138°C	0.067	0.056	0.022
As (iv), but after standing for 14 days	0.051	0.048	0.018

The figures for the more lightly vulcanized compounds (i) and (ii) show good agreement, but in the remaining cases a divergency between the polarographic and other results appears, which increases with the time of vulcanization, and which may be accounted for by the formation of reaction products between sulfur and some of the nonrubber components. Such products offer a varying degree of resistance to oxidizing agents, such as nitric acid, and appear to be decomposed by metallic copper (*cf.* sulfur-vulcanized oils), but remain unchanged by the base solution used in the polarographic process. Recent work carried out in this laboratory on the examination of the acetone extract shows that polarographic phenomena can be expected from a variety of minor components, notably zinc salts of fatty acids, and from some nonrubber fractions, and it is therefore important to note that, in this electrolyte, no polarographic wave was obtained from any other components of the rubber.

Interference from accelerators and antioxidants.—Proske has reported⁸, and it has also been shown in the laboratory, that certain antioxidants and accelerators of vulcanization exhibit polarographic activity. An exhaustive examination of all possible sources of interference of this nature is obviously impracticable, and study has therefore been confined to some of the commoner members of these classes of compounding ingredients.

Bloomfield⁹ has mentioned the formation of organic polysulfides during the the course of vulcanization of diphenylguanidine-accelerated stocks. Apart from direct polarographic interference which could arise, for example, from merging of the polarographic waves, some accelerators of vulcanization readily decompose into products which may include elementary sulfur, and it is possible that such decomposition could occur in the pyridine electrolyte. The substances examined and the degree of interference to be expected, as indicated by the half-wave potential, are presented in Table II.

The majority of the materials examined offer no interference to the sulfur wave; in fact in many cases the curve given by the accelerator itself is sufficiently regular in form to be suitable for measurement. Accelerators such as TMT appear to be stable towards the pyridine electrolyte, and it has also

TABLE II
POLAROGRAPHIC BEHAVIOR OF SOME COMMON ACCELERATORS AND ANTIOXIDANTS

Accelerator or antioxidant	Half-wave potential v. S.C.E.	Remarks on polarographic behavior
Diphenylguanidine (DPG)	Uncertain	No wave in pyridine electrolyte
D- <i>o</i> -tolylguanidine (DOTG)		No wave in pyridine electrolyte
Triphenylguanidine (TPG)		No wave in pyridine electrolyte
Hexamethylenetetramine (HMT)		No wave in pyridine electrolyte
Mercaptobenzothiazole (MBT)		Wave from zero volts and is completed before sulfur wave. Suitable for estimating accelerator
Benzothiazolyl disulfide (MBTS)	Uncertain	Wave from zero volts and is completed before sulfur wave. Suitable for estimating accelerator
Thiocarbanilide (TCA)	Uncertain	Wave from zero volts and is completed before sulfur wave. Suitable for estimating accelerator
Zinc isopropylxanthate (ZIX)	Uncertain	Wave from zero volts and extending beyond sulfur wave. Irregular shape in this electrolyte, unsuitable for measurement
Zinc diethyldithiocarbamate (ZDC)	-0.4	Sharp wave formed which does not interfere with sulfur determination. Suitable for estimating accelerator
Tetramethylthiuram disulfide (TMT)	-0.5	Behaves similarly to ZDC
Tetraethylthiuram disulfide (TET)	-0.55	Behaves similarly to TMT
Diphenylguanidine with derivative of mercaptobenzothiazole (Ureka)	-0.32, -0.5	Double wave suitable for estimating accelerator. No interference with sulfur
Diphenylguanidine phthalate with derivative of mercaptobenzothiazole (Ureka DD)	-0.33, -0.53	Similar to Ureka
Phenol-aldehydeamine type (Nonox-NSN)	-0.3, -0.97	Double wave of regular shape suitable for estimating antioxidant. No interference with sulfur wave
Nonox-HF	-0.3, -0.9	Similar to Nonox-NSN, but second wave poorly formed
Phenyl-2-naphthylamine (Nonox-D)	0.3	No interference with sulfur wave. Suitable for estimating antioxidant
Phenyl-1-naphthylamine (Nonox-A)	Uncertain	Wave from zero volts, completed before sulfur wave
Condensation product of aldol and aldol-2-naphthylamine (Nonox-S)	Uncertain	Poor wave form which does not interfere with sulfur determination
<i>s</i> -Di-2-naphthyl- <i>p</i> -phenylenediamine (Agerite White)	Uncertain	Poor wave which masks the sulfur wave
Piperidinium pentamethylenedithiocarbamate (PPD)	Uncertain	No interference with sulfur wave
Diphenylcarbamyl dimethyldithiocarbamate (ONV)	Uncertain	No interference with sulfur wave
Aldehyde derivative of a Schiff's base (A11)	Uncertain	No interference with sulfur wave
Reaction product of aniline with two different aliphatic aldehydes (A16)	Uncertain	No interference with sulfur wave
Reaction product of butyraldehyde and butylidene (A32)	Uncertain	No interference with sulfur wave
Triethyltrimethylaminetriamine (Trimene base)	Uncertain	No interference with sulfur wave
Benzothiazyl-2-monocyclohexyl sulfenamide (Santocure)	-0.52	Wave suitable for measurement

been established that heating TMT in acetone, as for example during the extraction process, does not give elementary sulfur.

Substances examined which interfere sufficiently seriously with the polarographic sulfur wave to render measurement of the latter doubtful include the accelerator ZIX and the antioxidant Agerite White. These investigations were, however, carried out at relatively high concentrations of the commercial materials added directly to the pyridine electrolyte. Restricted experience has shown that interference may be much less marked when these substances, or their decomposition products, occur in the lower concentrations given by acetone extraction of a typical vulcanized rubber.

The general question of the polarographic behavior of the minor components of vulcanizates, including accelerators and antioxidants, is being investigated in this laboratory, primarily with a view to their quantitative determination.

CONCLUSIONS

The polarographic method offers a rapid and accurate means of determining the "true" free sulfur in vulcanizates. In the case of single estimations, the test takes approximately as long as the copper-spiral method, but for multiple or replicate testing it is much quicker.

Since the determination is made directly on the acetone extract, it was necessary to examine at some length the possibility of interference from other ingredients of the extract. It is shown that most of the common accelerators and antioxidants are not likely to interfere, and promising methods of determining certain of these substances were revealed. Thus MBT, MBTS, TCA, A11, ONV, ZDC, TMT, TET, Ureka, and some of the Nonox series of antioxidants give regular polarographic waves readily distinguishable from that of sulfur, and the development of working processes for their determination should not present any great difficulties.

Other accelerators and antioxidants, notably ZIX, some Nonox antioxidants and Agerite White, while showing polarographic activity, give poor curves in the pyridine electrolyte. No doubt in other base solutions the form of curve could be improved, and their quantitative determination would then follow.

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DETERIORATION OF RUBBER UNDER THE INFLUENCE OF LIGHT AND DRY AND MOIST HEAT *

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INTRODUCTION

Although it is known that rubbers deteriorate more rapidly in tropical climates, little seems to have been done to determine the relative importance of the various factors likely to be involved, such as humidity, temperature, and light intensity.

It is essential to realize that tropical aging is not simply one condition, and this is brought out by a comparison of the deterioration of a typical rubber compound aged in both Abadan and Kuala Lumpur (see Table 2). Abadan is on latitude 27° N. on the Persian Gulf and has a hot, dry climate with clear skies; Kuala Lumpur is on latitude 3° N. near the West coast of Malaya and has a hot climate with daily heavy rains and a continually humid atmosphere. Both are tropical stations.

These facts suggest that aging tests used to simulate tropical conditions should include both dry and moist heat aging. It is the purpose of this paper to report experiments comparing Geer oven aging with moist heat aging and to compare both with actual deterioration in the tropics.

TEMPERATURES EXPERIENCED IN TROPICS

The theoretical maximum temperature attainable by articles exposed to sunlight is somewhere about the boiling point of water, how near depending on the value of the sun's radiation received. The highest temperatures recorded under various conditions in various parts of the world are summarized in Table 1.

The local factors which influence the temperature reached are many and varied. The size, shape, thermal capacity, and conductivity of the body will also influence the temperature of the body. If its shape is such that only a small part of its surface receives radiation, the rise in temperature will be slow and, because a greater surface is transmitting than is receiving radiation, the temperature will not go so high. A large thermal capacity and conductivity will not reduce the maximum temperature possible (except in so far as high conductivity may mean high conduction losses to other bodies) but will slow up the rise of temperature.

The color of the exposed surface also influences considerably the temperature reached, and black and dark colored surfaces cause a greater rise in temperature than white or light colored surfaces.

It would seem on balance that a temperature of at least 70° C will be reached for several hours per day by any exposed rubber and a temperature

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TABLE 1

Nature of surface	Place	Time of year	Temperature of Surface in °C	
			In shade	In sun
Dark upper surface ¹ of grounded aircraft	Tucson, Arizona	September	—	102
Thin black cloth ² under glass, 18 inches above ground	Madison, Wisconsin	June	—	82
Thin black cloth ² freely exposed, 18 inches above ground	Khartoum, Sudan	May	43	99
	Khartoum, Sudan	May	43	90
	Palestine ³	August	38	62
Surface of bare ground	Aguellal, Sahara ³	June	44	68
	Giza, Egypt ⁴	July	—	66
	Agra, India ⁵	May	43	69

The temperatures, originally given in °F, have been quoted to the nearest °C.

of 40° C by rubber sheltered from direct sunlight. This suggests that the normal Geer oven temperature of 70° C is a reasonable figure for comparative aging tests in a laboratory.

COMPARISON OF AGING AT ELEVATED TEMPERATURES (DRY AND MOIST HEAT) WITH NATURAL AGING IN THE TROPICS

Table 2 gives the results from physical tests on a tire tread type of compound, with and without antioxidant for both natural and accelerated aging tests. The results are expressed relative to values of 100 for the test results on the unaged material.

The conditions of tropical exposure were as follows:

In both localities the rubber samples were arranged under a shelter which protected them from the direct rays of the sun and from direct rainfall, but the rubber samples would, of course, still be in bright light, and the structure, consisting of a roof only, would not prevent driving rain from reaching the samples.

It is immediately apparent that the aging periods of ten and twenty-one days chosen were too long for proper comparison with six and twelve months'

TABLE 2

Compound	Conditions of Aging	TS	EB
A. Compound without antioxidant	6 months in Abadan	91	70
	12 months in Abadan	62	54
	6 months in Kuala Lumpur	85	74
	12 months in Kuala Lumpur	58	54
	Aged 10 days at 70° C	48	52
	Aged 21 days at 70° C	37	40
	Aged 10 days, 70° C, 100 per cent R.H.	34	48
	Aged 21 days, 70° C, 100 per cent R.H.	15	32
B. Compound with antioxidant	6 months in Abadan	110	82
	12 months in Abadan	90	80
	6 months in Kuala Lumpur	101	90
	12 months in Kuala Lumpur	84	82
	10 days at 70° C	89	86
	21 days at 70° C	73	67
	10 days at 70° C, 100 per cent R.H.	54	63
	21 days at 70° C, 100 per cent R.H.	26	45

natural aging; that moist heat causes greater deterioration than dry heat; and that the difference between the results from the dry (Abadan) and moist (Kuala Lumpur) regions is much less than the difference between the results from the dry and moist heat of the artificial aging.

These points are further emphasized by a review of the tropical and artificial aging of a number of compounds suitable for general mechanicals which were examined at the same time. Table 3 quotes merely the percentage tensile

TABLE 3

Compound	Initial tensile strength lbs./sq. in.	Abadan		Kuala Lumpur		Dry heat 70° C		Moist heat 70° C	
		6 m.	12 m.	6 m.	12 m.	10 d.	21 d.	10 d.	21 d.
1. White sheeting containing 43 per cent zinc oxide	2140	82	101	149	118	89	83	69	47
2. Red sheeting	1600	60	70	86	100	105	70	59	41
3. Black sheeting	1250	130	128	117	84	98	74	72	29
4. Black compound	1380	130	130	130	126	107	113	112	94
5. Black compound	2280	160	104	100	100	82	50	56	23

strength remaining and gives such details as are available of the compounds tested. As is frequent in production practice, the compounds were apparently not vulcanized to optimum tensile strength, to enhance their apparent aging properties by retaining a fairly constant strength over the earlier part of their useful life. Some of the compounds, therefore, show an increase in tensile strength after six months' natural aging but ten days at 70° C is, in general, too long for this effect still to be seen and either the strength has regained its initial value or there is a falling off.

The summary of the variation in tensile strength given in the Table does not bring out entirely the differences in the aging of the rubbers. The light colored rubber compound No. 1, aged in Abadan, showed deep sun crazing although it had not been exposed to direct sunlight, and resinous material was actually peeling from the sheet. Bending of the material caused deep cracking and difficulty was experienced in obtaining test-pieces. The maintenance of tensile strength after twelve months hides the fact that the material has a totally different surface when compared with its initial condition or with the same material aged in Kuala Lumpur.

DRY AND MOIST-HEAT ARTIFICIAL AGING

It was decided to investigate the relation between the effects of dry heat and moist heat under artificial conditions. No precautions were taken to protect the rubber from ordinary English north daylight during the handling necessary for testing. The conditions chosen were 70° C for all tests, but with one series were carried out without humidity control in a 70° C oven, and therefore obviously of fairly low humidity probably less than 10 per cent and a second with 100 per cent relative humidity produced by feeding live steam into the aging chamber. A third series repeated the second with the addition that air was continually fed into the chamber with the steam. The second and third series are, therefore, referred to as moist heat aging with restricted and free air, respectively. The samples stored in dry heat were examined after seven, fourteen, and twenty-one days and those in moist heat at seven and fourteen days.

The differences found between samples aged in moist heat with free and restricted air were scarcely significant though there was a tendency for the sample aged in free air always to give a lower tensile strength, and slightly lower elongation at break. The difference between moist and dry heat aging seems to be one of degree rather than kind, and it is possible to fit a conversion factor to the time scale and, hence, to superpose the tensile strength/time-of-aging curves. A figure of 1.85 seems to be an appropriate factor and Figure 1 shows the tensile strength of the compounds used after aging for the various periods, the aging periods of the compounds aged moist being multiplied by 1.85. The compounds used were as follows: A and B, as in Table 3, were tire tread type of compounds containing: smoked sheet, 100; zinc oxide, 5; stearic

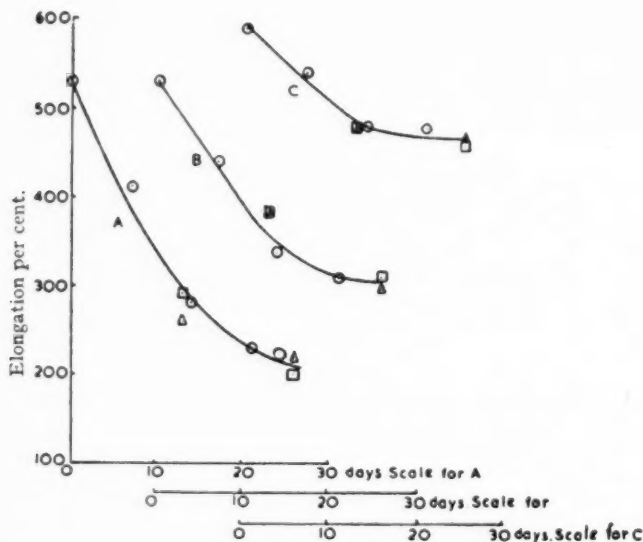


FIG. 1.

- Unaged and dry heat aged.
 ◻ Aged in moist heat with restricted air.
 △ Aged in moist heat with moving air.

acid, 2.5; MPC Black, 50; pine tar, 4.5; Santocure, 0.8; sulfur, 3. Compound A was without antioxidant; compound B contained one part of a proprietary antioxidant. Compound C was a sulfurless compound vulcanized with tetramethylthiuram disulfide (T.M.T.) and was as A but with 3 parts T.M.T. in place of Santocure and sulfur. For all three compounds, a single line represents fairly exactly the points for all three forms of aging. A similar graph can be drawn using the same factor 1.85 with the elongation at break, as is clearly shown in Figure 2. The modulus at 100 per cent extension rises to a maximum with aging and then falls and it is not so easy to be certain of the position of the maximum and the actual shape of the curve when only three points are available. However, Figure 3 shows the effect of a similar transformation with the same factor (1.85) as was deduced from, and then used with,

tensile strength and elongation at break. The curves give a reasonably good fit except that the differences between free and restricted air for the longer period of moist heat aging differ more for this property.

The evidence is, therefore, in favor of the statement that the presence of additional moisture, *i.e.*, the change over the humidity range from low humidity to 100 per cent R.H., accelerates the aging reaction or series of reactions without altering their nature, so aging for x days moist leads to exactly the same physical

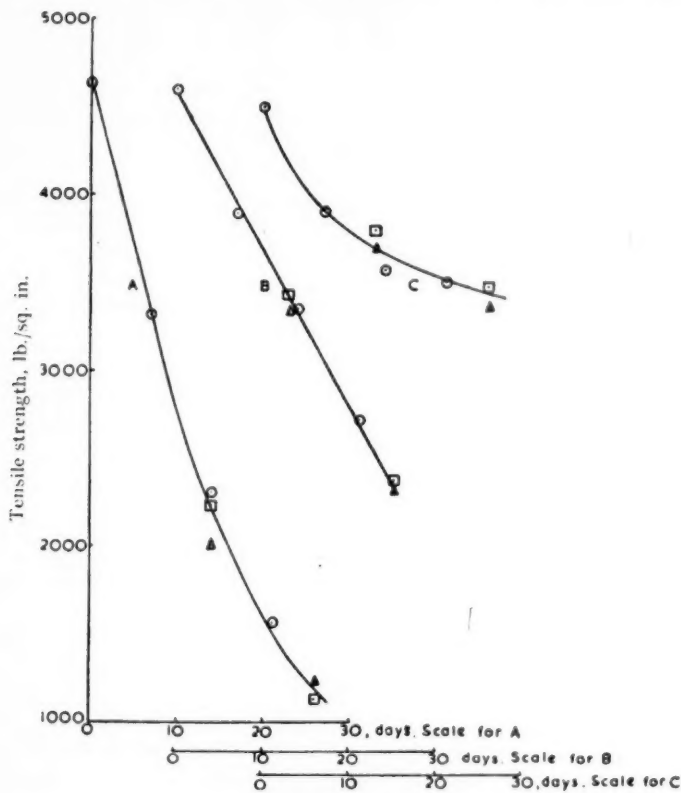


FIG. 2.

- Unaged and dry heat aged.
- Aged in moist heat with restricted air.
- △ Aged in moist heat with moving air.

properties as aging for y days dry at the same temperature, x and y being simply related such that x/y is constant, with and without antioxidant, and even when the compound is changed from one accelerated with a modified M.B.T., to one vulcanized by T.M.T. without sulfur.

At first it was thought that some simple physical explanation could be given for this in terms of the amount of swelling of the rubber, since, during moist heat aging, water absorption occurs up to quite large amounts (see

Table 4), even when the water absorption of the initial compound unaged is very small. That there is no correlation can be seen from Table 4 where additional results for tensile strengths are given for rubber derived from pale crepe and latex. The water absorption found at the stages of the aging are also given and compared with compound A previously reported.

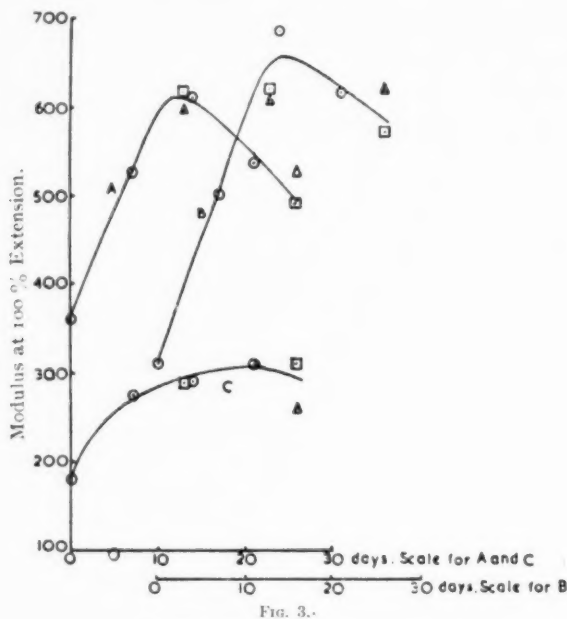


Fig. 3.
 ○ Unaged and dry heat aged.
 □ Aged in moist heat with restricted air.
 △ Aged in moist heat with moving air.

TABLE 4
 PERCENTAGE TENSILE STRENGTH REMAINING AND PERCENTAGE WATER ABSORPTION

Compound based on	Initial water absorption	7 days in moist heat		14 days in moist heat	
		% tensile strength	% water absorption	% tensile strength	% water absorption
Smoked sheet (A)	0.5	43	3.9	27	7.9
Pale crepe	1.5	38	7.6	31	12.6
Latex	1.7	43	9.1	27	15.6

EFFECT OF LIGHT

The general aging effect so far discussed has been a reduction in tensile strength and elongation at break. This is caused by scission of the long hydrocarbon chains of the molecules. Some cross-linking does, however, occur at the same time, and the net result is due to the balance set by these two opposing processes. The occurrence of cross-linking manifests itself by the increase in modulus in the early stages of aging, and is illustrated in Figure 3.

It is presumed that these reactions occur throughout the mass of the rubber. The appearance of the rubbers actually aged in the tropics shows that reactions which occur predominantly at the surface are more important at Abadan than at Kuala Lumpur.

The oxidative nature of light stiffening, which is probably only an early stage of sun crazing, has been recently discussed⁶. This paper showed conclusively that oxygen as well as light was essential and that the chemical nature of the rubber surface becomes very greatly modified during the process. For instance, all trace of unsaturation disappears from the molecule. The general sequence of reaction which occurs is discussed, and those interested are referred to the full paper. It suffices here to state that only the surface is affected by the light catalyzed reaction and that it leads to very considerable cross-linking and, hence, increase in modulus.

TECHNOLOGICAL DISCUSSION

It will have been obvious from foregoing sections of this paper that recommendations relating to the use and storage in, and testing rubber for, tropical countries depend on the nature of the article. Where the surface layers of the rubber may be said to form a substantial part of its weight, as for example, in rubber proofings, the deterioration is light catalyzed and it is this stiffening

TABLE 5

Number of hours' exposure to carbon arc	Relative modulus	Typical equivalent days
0	1	0
25	5.55	10
50	8.4	18
75	15.9	30
100	27.0	35

and subsequent crazing of the surface that is the immediate cause of failure. Where rubber is used more in bulk then thermal and moisture effects become more important.

Thin proofings.—The use of a dark pigment filler⁵, though it will tend to raise the average temperature of the article, will reduce the penetration of light and hence limit the depth to which light-catalyzed oxidation readily occurs. Storage in the tropics, or in bright sunlight generally, will result in less deterioration if the articles are packaged in opaque coverings. If, for display purposes, this is not possible, then recourse should be had to suitably dyed wrappers. Earlier work¹ has shown that mercury-vapor lamps do not produce other than slight deterioration and display lighting and fluorescent lamps are unlikely to damage even thin articles except as they may affect organic dyestuffs by causing them to fade.

The problem of an accelerated light aging test, particularly for proofings or proofing compounds, is best tackled by the use of the cantilever modulus test described by Newton and Wake⁶, together with an arc lamp or the use of direct sunlight. The authors are indebted to C. M. Blow for drawing their attention to the fact that to simulate sunlight a continuous emission spectrum is required, such as is given by the carbon arc and unlike the line spectra of mercury-vapor lamps, so that adequate energy can be radiated. The exposure of a standard 2-oz. proofing to sunlight and to the carbon arc was carried out to confirm this. Table 5 shows the increases in stiffness which occurred in the sample

exposed to the carbon arc, together with the equivalent number of days' exposure to bright sunlight in August, 1949. The proofing used was a yellow, heat-vulcanized compound based on natural rubber. The modulus measurements were made by a simple device, using the specimen as a cantilever¹. The exposure to the carbon arc was in a Fugitometer and was made for us by C. M. Blow.

The best accelerated test for use by manufacturers is the preparation of a very light-weight proofing, say 2 ounce, on a very light material, *e.g.*, parachute nylon, from the compound to be tested. This should be exposed to a carbon arc and the modulus increase measured by the cantilever apparatus referred to. Measurements would probably be conveniently made after exposures of 10, 20, 40, and 80 hours. If a carbon arc is not available, spring or summer sunshine is sufficient (in southern England) to produce substantial stiffening in an exposure of about a week. It is obvious that a comparison with a control will always be necessary.

Other rubber articles.—The aging of rubber articles containing bulk rubber rather than a thin layer is largely a question of thermal aging. It has been shown that the differences between rubber exposed in Abadan and Kuala Lumpur are less than the differences between the same rubber aged dry and aged moist. It has also been shown that the relation between dry and moist heat aging, at any rate for fairly simple compounds, is itself simple. There seems, therefore, but little incentive to use the more troublesome moist heat aging chamber instead of the Geer oven. However, until evidence from a wider range of compounds is forthcoming, many technologists will prefer to test separately the behavior of their compounds in moist heat.

In use and in storage, articles should, where possible, be stored or mounted in use away from the ground or wall, so that air circulation around them is possible; *e.g.*, cables and wires should be mounted in the shade, but spaced from the supporting wall or ground. Light colors rather than dark colors are to be preferred with the proviso that, if surface properties are important, the reverse preference should hold.

SUMMARY

A comparison has been made of the aging of rubber compounds under tropical conditions. Two localities were chosen, one of which has a dry climate, the other heavy rainfall and high humidity. The results are compared with those obtained by ordinary Geer oven aging and by aging at the same temperature, but with 100 per cent relative humidity. This artificial moist heat aging is found to be much more severe than the tropical moist aging, but it is not different in kind to aging in a Geer oven and a simple conversion factor can be used to transpose results. Samples aged under dry conditions in the tropics are more influenced by bright sunlight, even though shielded from its direct rays, than by the heat aging. Recommendations are made concerning both the use of materials in the tropics and methods of accelerating aging to assess their behavior in the tropics.

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STUDY OF THE MECHANISM OF SURFACE DETERIORATION OF EBONITE AND OF MEANS OF PREVENTING DETERIORATION *

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1. INTRODUCTION

The work to be described extends that of Church and Daynes¹ and other workers on the mechanism of the surface deterioration of ebonite and methods of minimizing the effect.

Church and Daynes obtained curves of log surface resistivity against period of exposure similar in shape to curve A in Figure 1, showing a horizontal portion, followed by a portion falling steeply to a relatively constant value. This behavior was ascribed to the formation of sulfuric acid in droplets on the surface, the initial horizontal portion corresponding to isolated droplets which subsequently link up to form a continuous conducting film. However, it has recently been found^{2,3} that, for exposures to light from a mercury vapor lamp, the initial horizontal part of the curve disappears, and curves similar to curve B of Figure 2 have been obtained. In Section 3 of this paper, this difference is confirmed, and various possible explanations are considered. In Section 4 the variation of resistance with period and conditions of storage after exposure is examined to provide further information about the mechanism of deterioration. After a discussion of certain chemical aspects of the problem, and some data on loaded ebonites, the paper concludes with a discussion of possible methods of preventing or reducing the formation of an acid film.

2. EXPERIMENTAL METHODS

The methods of exposure of specimens and measurement of surface resistivity used in this investigation were similar to those of Church and Daynes¹. Strips of cleaned ebonite with colloidal graphite electrodes were mounted in glass tubes containing a little moist sodium chloride to maintain a relative humidity of 75 per cent. The method described more recently³ of exposing several specimens in a box with a quartz lid has been found to give rather erratic results, and the original method is to be preferred. Ordinary medium-hard glass tubes were used, as preliminary tests established that Vitaglass tubes did not cause a greater rate of deterioration.

Surface resistivity was measured using a Lindemann electrometer in the manner of Church and Daynes¹, except that, to increase the accuracy of measurement, the voltage on the specimen was increased to 500 volts and the time of electrification before measuring resistivity was increased to 5 minutes.

All exposures were to artificial light, either to a tungsten filament lamp or to a quartz mercury vapor lamp. Except for the tests on loaded ebonites in

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Section 5, all specimens were of a 68/32 rubber-sulfur ratio unaccelerated natural-rubber ebonite vulcanized for 7 hours at 155° C. Tests on different samples of the same composition and vulcanized for the same period gave closely similar deterioration curves.

3. THE INFLUENCE OF TYPE AND INTENSITY OF ILLUMINATION ON SURFACE DETERIORATION

Three specimens of unloaded ebonite were exposed at various distances from a 150-watt tungsten filament lamp. They were removed from the light at intervals, stored in the dark for two days to avoid the short period changes of resistivity discussed in Section 4, and their resistivities were then measured. In Figure 1, the logarithm of the resistivity is plotted against a function pro-

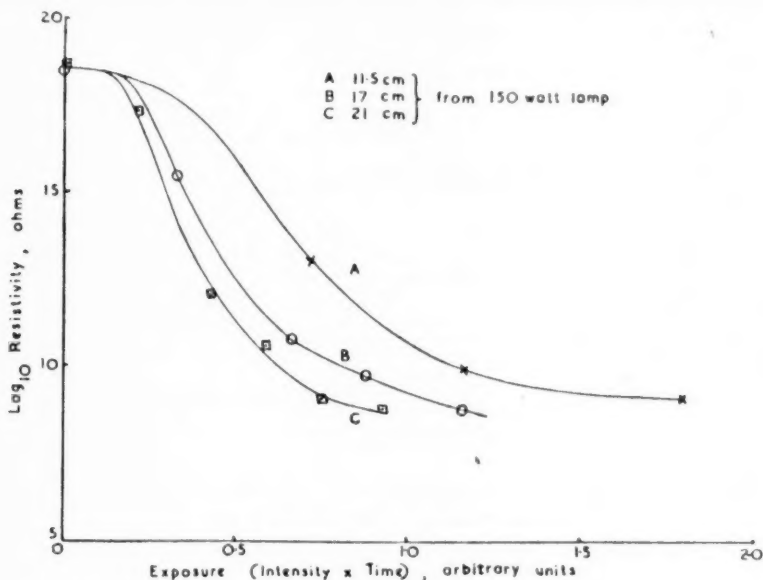


FIG. 1.—Variation of surface resistivity with exposure to a 150 w. tungsten filament lamp.

portional to the product of intensity of illumination and period of exposure, *i.e.*, to the quantity of light falling on the specimen. It will be seen that the decrease in resistance caused by a particular quantity of light falling on a specimen is less the greater the intensity of illumination; although the actual rate of decrease of resistance of a specimen is increased as the specimen approaches the lamp, it does not increase as rapidly as the light intensity.

Figure 2 shows similar results for exposures at two distances from a mercury vapor lamp, and again the effect of a given amount of light is less, the closer the specimen is to the lamp. Also the curve for exposures at 45 cm. (curve B), and to a lesser extent curve A, starts falling rapidly even for short exposures. This confirms the possibility of exposure conditions giving a curve lacking an initial horizontal part, mentioned above. It will be seen that, by varying the

exposure conditions, a continuous transition is possible from the shape of curve A in Figure 1 to the shape of curve B in Figure 2.

Curve A in Figure 3 shows the effect of interposing a Wratten No. 23 gelatin filter, transmitting only yellow, red, and infrared radiation between the tungsten lamp and a specimen after deterioration had begun. The specimen resistance rose instead of continuing to fall. Curve B shows that a No. 16 filter, which transmits in addition green light, keeps the resistance approximately constant. Curve C shows that if, after a fairly long exposure, the specimen is reversed for a short time (not long enough for the second side to reach a resistivity low enough to affect the measured resistance), the resistance of the face first exposed rises. The early parts of the curves do not coincide because the distance of the specimen from the lamp and the initial resistivity were different in each case. As a final variation, a specimen was exposed 18 cm. from a tungsten filament lamp with a layer of water 1 cm. thick between lamp

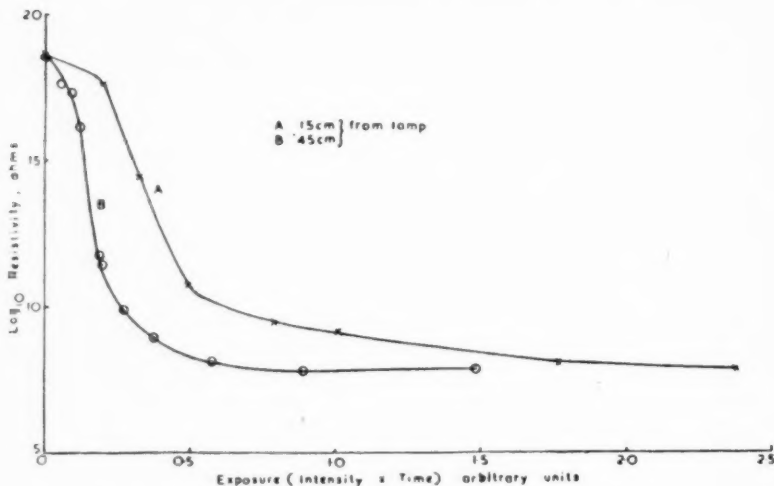


FIG. 2.—Variation of surface resistivity with exposure to a mercury vapor lamp.

and specimen. In spite of losses by reflection at the surfaces of the water and the glass container, the specimen resistance fell more rapidly than with no such water screen.

The decrease of the efficiency of the light in causing deterioration with increase of the intensity of illumination may be due to a decrease in the rate of formation of acid by breakdown of the surface, or to an increase in the rate or removal of the final product (or an intermediate product) from the surface. The second possibility is discussed more fully in the next section, but at this point it may be noted that this mechanism appears necessary to explain the change in shape of the curves with intensity of illumination, and the increase in resistance of specimens when reversed. If the rate of removal of acid increases rapidly with temperature, curve B, in Figure 2, with the specimen only slightly above room temperature and with a rapid rate of deterioration, may be taken as approximating to the characteristic deterioration curve.

Exposure with the specimen temperature higher (curve A in Figure 1), or at a much slower rate (for example, the daylight results of Church and Daynes¹, which must have extended over several days), causes an initial horizontal portion on the curve, since acid is removed from the surface at nearly the same rate as it is formed. A No. 23 Wratten filter, which cuts out all radiation of wave length less than 5700 Å, apparently stops the formation of acid more or less completely, but since most of the heating of the specimen is by red and infrared radiation, the temperature remains high enough to cause removal of acid. A No. 16 filter, cutting out all wave lengths less than 5200 Å, appears to balance the deterioration rate against the recovery rate, while a water

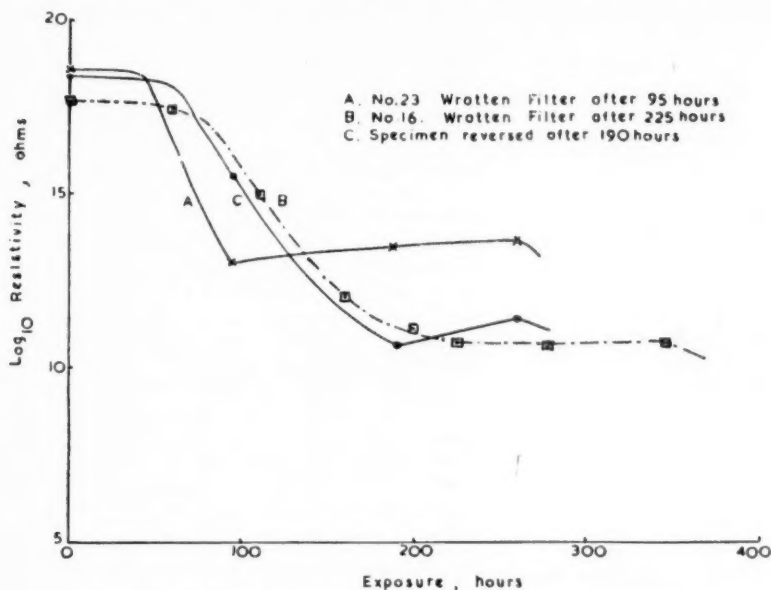


FIG. 3.—Influence of filters and reversal on rate of deterioration (tungsten filament lamp).

screen, by absorbing the long wave length radiation, rather than the shorter wave lengths, increases the deterioration rate relative to the recovery rate.

Although a recovery effect (loss of acid) certainly occurs, there is some doubt whether this alone is adequate to explain the large changes in deterioration rate observed (see Section 4 below). It is likely that the amount of acid formed by a definite quantity of light is lower at higher temperatures, because the amount of oxygen adsorbed on to the surface probably would be reduced, and the amount of moisture adsorbed is certainly reduced.

4. VARIATIONS IN RESISTIVITY ON CEASING EXPOSURE

The resistance of unloaded ebonite on ceasing exposure varies, in general, in two stages. The resistance falls for a time and then rises, fairly rapidly for a few days, then slowly. The initial drop is most marked where the heating effect has been greatest, as for exposure close to a tungsten lamp (Curve C,

Figure 4). The drop is reduced by exposure with a water screen interposed (Curve B), and after exposure 45 cm. from a mercury vapor lamp, the initial drop does not occur at all (Curve A). Since the temperature of the specimen during exposure will be higher than that of the salt solution (which is shaded), it is to be expected that some drying out of the surface will occur, and humidity effects appear to account quite adequately for the observed short period variation. To confirm that it sometimes takes over 24 hours for the surface to reach equilibrium with the surrounding atmosphere, a check on the time taken for a partially dried-out film to reach equilibrium with an atmosphere at 75 per cent relative humidity was obtained by storing a deteriorated specimen in an atmosphere of very low humidity (dried with phosphorus pentoxide), and then inserting sodium chloride solution in place of the phosphorus pen-

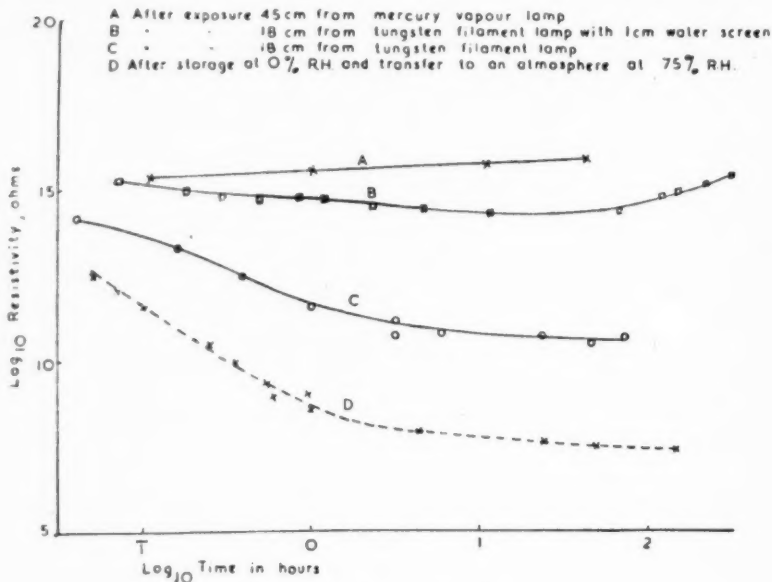


FIG. 4.—Variation of surface resistivity during storage.

toxic. Curve D in Figure 4 shows the variation of the resistivity with time after inserting the salt solution, and it can be seen that the time taken to reach equilibrium under the changed conditions is about 48 hours. The reason for this may be that some acid is absorbed a short distance into the surface and that it takes some time for the condensed water to penetrate to the innermost part of the acid.

An eventual increase in resistance, after these humidity effects had ceased, was found to occur to some extent whatever the method or period of exposure, but the rate of recovery of resistance depended on the method of exposure and temperature of storage. Figure 5 shows the resistivity curves, after the first day, of two specimens stored in the dark at room temperature (10° to 15° C). Curve A is for a specimen exposed for 7 hours, 15 cm. from a mercury vapor lamp, while curve B is for a specimen exposed 90 hours, 18 cm. from a 150-watt

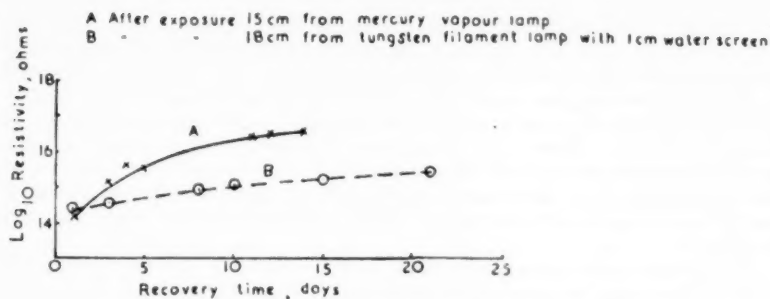


Fig. 5.—Recovery of surface resistivity during storage in dark.

tungsten filament lamp (with 1 cm. water screen). The specimen with a short exposure recovered rapidly to a resistance not very far below its resistance before exposure, whereas the specimen exposed for a much longer period to reach the same resistivity recovered only slightly.

Table 1 shows the amount of recovery of specimens at various stages of deterioration stored for about five days at various temperatures. The specimens were exposed, conditioned 24 hours at room temperature, measured, then stored at the stated temperatures, and remeasured after 24 hours at room temperature. It will be seen that the recovery rate is sharply temperature dependent. The slight drop in resistance for some specimens stored at 0° C and at room temperature was probably due to insufficient conditioning before measurement. This was limited to 24 hours to prevent recovery of the specimens at room temperature masking the results, as the error involved is not important compared with the large recovery at 25° C. The recovery is not as great as in Figure 5, as the specimens were exposed for a number of short periods, with recovery between exposures, instead of for one period only, as for the results in Figure 5.

To evaluate the importance of these recovery effects on the shape of the deterioration curve, it is necessary to estimate the surface temperature of the specimen during exposure. A fine iron-constantan thermojunction was mounted on the surface of a specimen, which was of the usual type, except that

TABLE I
CHANGE OF RESISTIVITY OF SPECIMENS STORED AT VARIOUS TEMPERATURES

Storage temperatures	Log ₁₀ resistivity		Period of storage (days)
	Initial	Final	
0° C	15.7	15.4	4
	14.4	14.2	5
	12.8	12.5	5
	8.8	9.0	7
10° to 15° C	15.3	15.2	4
	14.1	14.0	5
	11.9	11.8	5
15° to 20° C	8.2	8.7	7
25° C	15.2	16.2	4
	14.4	15.3	5
	12.7	14.0	5
	8.0	8.6	7

the support wires were of iron and constantan (to be used as leads from the thermojunction), and the specimen surface was filed slightly convex, so that the junction was drawn tightly against the ebonite. The difference, measured in this way, between the equilibrium surface temperature with the lamp on—reached in about 30 minutes—and the temperature before switching on, is shown in Table 2. These results are not very accurate, but give an idea of the surface temperature. It will be seen that the assumption in Section 3, that the temperature of the specimen was not greatly changed by interposing a filter to cut out only the shorter wave lengths, or reversing the specimen, was justified.

The above results agree qualitatively with the theory put forward in the last section, explaining the changes in resistivity-exposure curves by a recovery of resistance taking place simultaneously with the deterioration. However, curve A in Figure 5 suggests that the recovery rate immediately after exposure (if short period effects could be eliminated) would not be greater than a factor 10 in a day, and although the rate might be considerably greater at 300° C, it seems unlikely that the observed difference in the deterioration by a certain

TABLE 2
SURFACE TEMPERATURE OF EBONITE DURING EXPOSURE

Type of lamp	Exposure conditions	Temperature rise in ° C
Mercury vapor	15 cm.	19
	45 cm.	1.5
Tungsten filament	11.5 cm.	24
	21 cm.	9
	17 cm. { No filter	18
	{ No. 16 filter	17
	{ No. 23 filter	14
	{ Specimen reversed	16

quantity of light between a specimen 15 cm. from the mercury vapor lamp (at this temperature) and a specimen 45 cm. from the lamp, could be accounted for. The specimen 15 cm. from the lamp took only 13 hours to reach a resistivity of 10^{10} ohms. Other reasons for the differences in deterioration rates have been discussed in Section 3.

The reason for the recovery of resistivity of stored specimens may be the removal of sulfuric acid from the surface by diffusion, or by neutralization by some basic constituent. Since the recovery rate becomes very slow after a few days, dispersal of acid by diffusion is probably of only secondary importance, and since the addition of about 20 per cent of various basic fillers (including calcium and barium carbonates) has been shown⁶ to have little effect, removal of acid by neutralization is probably also unimportant. The most likely explanation is that sulfurous acid is formed as an intermediate compound, and in time partly oxidizes to sulfuric acid and partly decomposes to sulfur dioxide and water. At higher temperatures a larger proportion of sulfurous acid decomposes, so the effective deterioration rate is reduced. On storage in the dark, little further oxidation occurs, since oxidation occurs only slowly without light, and the resistance gradually rises to a maximum, as the sulfurous acid decomposes, and sulfuric acid alone remains.

The difference in the recovery shown by two specimens having approximately the same initial resistivity (Figure 5) is now readily explained. Curve A refers to a specimen exposed for a short time to a mercury vapor lamp. On

ceasing exposure, a large proportion of the acid present is sulfurous acid, which decomposes in a few days. Curve B refers to a specimen exposed for a much longer period, at about the same temperature, to a tungsten filament lamp, and during the exposure some of the sulfurous acid formed was oxidized, while some decomposed, so recovery on ceasing exposure was slight, since the film was now almost entirely sulfuric acid.

It would seem that, after ten days, little sulfurous acid remains, but a very slow recovery continues for at least 50 days, probably due to diffusion. The influence of storage temperature on the proportions of sulfurous acid decomposed or oxidized was shown clearly by exposing two specimens simultaneously so that each, after 24 hours' conditioning at room temperature, had a resistivity of 5×10^8 ohms. One specimen was then stored at 35°C for ten days, and, after conditioning at room temperature, its resistivity was 3×10^{11} ohms, while the other specimen, stored at room temperature for the same period, had increased in resistivity only to 2×10^9 ohms. Subsequent storage of this specimen at 35°C had little effect, showing that ten days' storage at room temperature leaves little sulfurous acid unoxidized.

5. CHEMISTRY OF FILM FORMATION

In view of the smallness of the quantities involved, and the present very limited knowledge of the detailed structure of ebonite, only indirect evidence of the nature of the deterioration is obtainable.

It has been reported previously that the surface film consists of sulfurous and sulfuric acids⁶, and that the total quantity of acid¹ on a standard specimen 2.5 sq. cm. in area of resistivity 10^7 ohm was about 5×10^{-6} gram. In the present tests, microscopic examination of the droplets led to a value of about 3×10^{-3} gram of acid for a specimen of this resistance. A pH determination on washings from a specimen of resistivity 10^8 ohm, using a potentiometer and standard electrodes, was compared with the value for an unexposed specimen, and gave a value 3×10^{-4} gram for the weight of acid. Thus the value previously given for the amount of acid is probably at least 100 times too small. If the acid formed a uniform layer, the apparent surface resistivity would be less than the observed value by a factor 10^4 .

With regard to the chemical nature of the washings, a distinct turbidity could be obtained with barium chloride solution, with or without the addition of hydrochloric acid, confirming the presence of sulfuric acid.

The origin of the sulfur in the sulfuric acid must be either free sulfur or the rubber-sulfur compound. The deterioration has been shown to occur in the absence of free sulfur⁶, and, in any case, elementary sulfur is not oxidized in these conditions, so the rubber-sulfur compound is the primary source of the acid.

The exact nature of the rubber-sulfur compound is not of importance, as the use of accelerators with natural rubber ebonites has little effect⁷, and synthetic rubber ebonites deteriorate as rapidly, or more rapidly, than natural-rubber ebonite⁸. It is, of course, possible that some group common to all these compounds is the unit active in deterioration.

It has been shown⁹ that, when ebonite is exposed to sunlight, hydrogen sulfide is evolved, and it has hitherto been assumed, *e.g.*, by Porritt¹⁰, that the oxidation of hydrogen sulfide was the source of the sulfuric acid. There is no evidence to support this hypothesis, and it seems rather improbable, as the principal product of the oxidation of hydrogen sulfide by air, water, and light is elementary sulfur, although sulfuric acid may also be formed. Thus it is

to be expected that some sulfur would be visible when sufficient acid had been formed to be visible, but there is no sign of sulfur on a surface exposed to light long after the acid is first seen.

It was found that a specimen of unvulcanized ebonite exposed in an atmosphere of hydrogen sulfide, oxygen, and water vapor did not decrease in resistivity even after prolonged exposure to a mercury vapor lamp, giving further confirmation to the suggestion that hydrogen sulfide is not concerned in the deterioration.

The first factor necessary for the deterioration is light. The results in Section 3 show that only light of wave length less than 5700 Å has any detectable effect, and that light in the region 5700 to 5200 Å has only a slight effect, in spite of the fact that only about 1 per cent of the radiation from a tungsten filament lamp has a wave length less than 5200 Å. A more detailed study of the influence of wave length on the rate of deterioration would probably not be of value, not only because of the difficulty in obtaining equal specimen temperatures during exposures to wave length bands with equal deteriorating power, but also because the complexity of the ebonite structure makes it unlikely that useful deductions could be made.

The influence of moisture on the rate of deterioration has been determined previously¹. It was shown that the rate of deterioration is greatest at between 75 and 90 per cent relative humidity, the higher value being for the early part of the deterioration. This can be explained by supposing that water, oxygen, and ebonite are necessary simultaneously to form acid, and the reaction takes place only where water and oxygen are adsorbed side by side on the ebonite surface. Thus excess water, or lack of water, reduces the deterioration rate. Owing to absorbed oxygen and water in the average specimen, it is at present not possible to say whether the complete elimination of either would stop the reaction completely, but it would seem likely that such is the case. As some acid is formed, it absorbs some water, so that the relative humidity necessary to keep the optimum ratio of water to oxygen at the surface is reduced. Also, further deterioration will tend to take place at the boundaries of the droplets first formed, which may account, at least in part, for the extremely uneven final distribution of acid.

It has been shown¹¹ that stability decreases with increase in vulcanization coefficient. This is consistent with the assumption that the rate of deterioration increases with the number of rubber-sulfur bonds in the surface. Results of some tests on loaded ebonite can also be interpreted on this basis. It was found that a selenium-loaded ebonite deteriorated at about half the rate of an unloaded ebonite; from the degree of loading it was estimated that the number of rubber-sulfur links per unit area of surface was probably less by a factor of about two. A commercial loaded ebonite showed little advantage over an unloaded ebonite in rate of deterioration.

6. POSSIBLE METHODS OF PREVENTING DETERIORATION

It has been shown that the rubber-sulfur compound in ebonite, in the presence of air, moisture, and light, forms sulfuric acid, with sulfurous acid a probable intermediate compound. The sulfurous acid is partly converted to sulfuric acid, and partly decomposes, while the sulfuric acid may diffuse very slowly into the ebonite.

The most obvious method of preventing deterioration is by coating the surface in some way, and several types of coating have been tried. Only coatings of reasonably high resistance, and which are unlikely to be easily

scratched, are of interest. A thin layer of polystyrene (only slightly permeable to air and moisture) was useless, possibly because of absorbed oxygen and moisture in the ebonite. A wax film, which might have been expected to prevent the formation of a continuous film of acid, was also useless. A Bakelite layer 1 mm. thick, excluding light as well as restricting the access of air to the surface, was completely effective, except that the Bakelite itself gave an effective surface resistivity of only 10^{11} ohms. Since some grades of Bakelite themselves drop considerably in resistivity on exposure to light¹², and since application of the coating involves baking, the method is not suitable for all products.

Incorporation of a basic material (to neutralize the acid) in the ebonite was not found to be useful⁵ except, possibly, in circumstances where the rate of formation of acid was very slow. Thus, such a material in the coating or the ebonite might be useful as a secondary protection when a surface coating is used.

It was thought that, provided a compound could be found to withstand the vulcanization conditions necessary for ebonite, incorporation of an anti-oxidant might reduce the deterioration rate. Mixes of smoked sheet 6S (parts by weight), sulfur 32, and antioxidant 3, were press-vulcanized for 4 hours at 155° C. The antioxidants chosen were representative of the chief types used in rubber, and are listed in Table 3. Exposures were made in the usual way

TABLE 3

Antioxidant	Resistivity before exposure (ohms $\times 10^{17}$)	Hours' exposure to reach		Final resistivity (ohms $\times 10^{15}$)
		10^{15} ohms	10^{12} ohms	
None	2.5	130	195	0.3
Phenyl- α -naphthylamine	10	135	210	0.1
Phenyl- β -naphthylamine	2.5	180	240	1 (or less?)
Aldol- β -naphthylamine	3	180	230	3
<i>p</i> -Aminodiphenyl-acetone condensation product*	4	190	260	1
Quinol	0.3	200	300	3
<i>p</i> -Aminophenol	1	300	550	100 (or less?)
<i>sym.</i> Di- β -naphthyl- <i>p</i> -phenylenediamine†	0.4	480	750	3000

* Santoflex.

† Age-Rite White.

at 16 cm. from a 100-watt tungsten filament lamp. The deterioration curves were all similar to curve A in Figure 1, and Table 3 gives the exposure periods needed to reach 10^{15} and 10^{12} ohms, and the final value of surface resistivity after very considerable exposure.

All the ebonites containing antioxidants appeared more stable than the control without antioxidant, but only the last 3 or 4 of those in Table 3 gave a substantial improvement. The protective effect of *sym.*-di- β -naphthyl-*p*-phenylenediamine was confirmed by exposures to a quartz mercury-vapor lamp; the antioxidant increased the period required to reach 10^{11} ohms by about $2\frac{1}{2}$ times.

The three most effective antioxidants are compounds that can form semi-quinones; such compounds are known strongly to influence oxidation-reduction reactions¹³. It would be unsafe to conclude from these experiments that all such compounds will be effective antioxidants for ebonite, but the observation does suggest a line of approach, if it is considered worth while developing special antioxidants for this purpose.

Reduction of the number of rubber-sulfur bonds in the surface by chemical treatment, by reduction of the vulcanization coefficient, by dilution with a

filler, or in any other way is unlikely to produce a worth while improvement without seriously altering the properties of the ebonite. It is just possible that some nonsulfur vulcanization method could be found to produce an ebonite, but this has not so far been reported.

To sum up, it appears that most of the methods which have been suggested for reducing the deterioration of the surface of ebonite have been tried, either previously or in the present work, and found inadequate. At present a surface coating appears to be the only method likely to be capable of useful application, and this method can be applied only where it is permissible to reduce the initial surface resistivity to a relatively low value, and to alter the appearance of the surface. Certain antioxidants reduce the deterioration rate, but so far no antioxidant has been found sufficiently effective to avoid the necessity for a surface coating.

SUMMARY

Following up earlier work on the subject, experiments are reported showing that the deterioration of the surface resistivity of ebonite caused by a particular quantity of light increases with decreasing intensity of illumination, and from the results of exposures to different types of radiation it is concluded that the surface temperature of the ebonite during exposure is the most important variable causing this difference. The observed effects are explained by assuming that sulfurous acid is produced as an intermediate product in the deterioration, and that this may either decompose to sulfur dioxide and water, or oxidize to sulfuric acid. If the former reaction is favored by a rise in temperature, the observed influence of intensity and type of illumination, and also the changes in resistivity after ceasing exposure can be explained.

Possible methods of preventing or reducing deterioration are discussed, and it is concluded that application of an opaque surface coating, possibly incorporating a suitable basic material to neutralize any acid formed, is the only method likely to be really effective. This method is not possible in many cases. Incorporation of a suitable antioxidant (*sym.* di- β -naphthyl-*para*-phenylenediamine was the best of those tested) reduced the rate of deterioration. Where surface coating is impracticable, the use of an antioxidant might be considered, although improvement of resistance to deterioration by a factor of more than three has not so far been achieved by this means.

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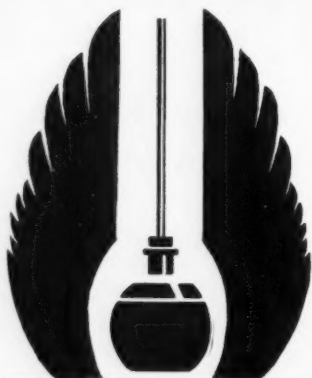
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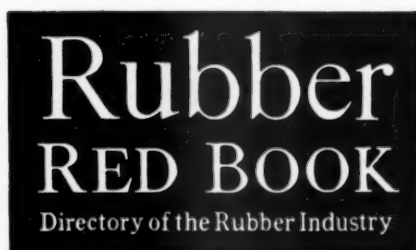


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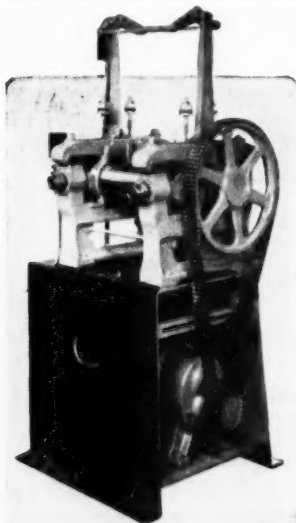
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